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Environmental Aspects of Chemical Use in Printing Operations

Research Triangle Inst.

Prepared For
Environmental Protection Agency

January 1976

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ENVIRONMENTAL ASPECTS OF CHEMICAL USE IN PRINTING OPERATIONS

(SEPTEMBER 22-24, 1975, KING OF PRUSSIA, PA.)

CONFERENCE PROCEEDINGS

OFFICE OF TOXIC SUBSTANCES
ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

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This conference was the last in a series of three on the environmental impact of chemicals in various industrial operations.

The objective of this conference was to cover and discuss current chemical use, functions of chemicals in the operations, byproducts likely to be introduced, known health or environmental contamination. More specifically, papers were presented and discussions held that covered industrial emissions and effluent surveys, chemicals and their effects, reclamation and disposal and academic programs.

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(September 1975, King of Prussia, Pennsylvania)

CONTRACT NO. 68-01-2928

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OFFICE OF TOXIC SUBSTANCES
ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

Prepared for

OFFICE OF TOXIC SUBSTANCES
ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

January 1976

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FOREWORD

The proceedings for the conference on "Environmental Aspects of Chemical Use in Printing Operations" is the third of three reports, each on a different conference, to be submitted under Contract No. 68-01-2928 to the Office of Toxic Substances for the Environmental Protection Agency. The conference was held at the Holiday Inn – Valley Forge, King of Prussia, Pennsylvania, on 22-24 September 1975.

The objective of this conference was to cover and discuss current usage of chemicals in the printing industry, the byproducts thereby introduced, the known health or environmental effects from chemicals used, and the measures undertaken or available for use in controlling environmental contamination. More specifically, papers were presented and discussions held which covered types of printing processes, emissions regulations, and health hazards from printing effluents.

Dr. Farley Fisher, Chief, Early Warning Branch, Office of Toxic Substances, Environmental Protection Agency, Washington, D.C., was the Project officer and General Chairman of the conference.

Mr. Franklin A. Ayer, Manager, Technology and Resource Management Department, Center for Technology Applications, Research Triangle Institute, Research Triangle Park, North Carolina, was the Conference Coordinator and Compiler of the proceedings.

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Opening Session

Farley Fisher, Ph.D.[*]
General Chairman

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[*] Chief, Early Warning Branch, Office of Toxic Substances, Environmental Protection Agency, Washington, D.C.

OPENING COMMENTS

Farley Fisher, Ph.D.
General Chairman

I would like to welcome you all to the opening of the conference on Environmental Aspects of Chemical Use in Printing Operations sponsored by the Office of Toxic Substances of the Environmental Protection Agency.

I am Farley Fisher, Chief of the Early Warning Branch of the Office of Toxic Substances of EPA. I am going to be your general chairman here, which means I am pretty much of a figurehead.

However, since I am largely responsible for setting up this snowball, which has developed into this conference, let me say just a few words about why we decided to hold this conference and what we hope to accomplish.

The mission of the Early Warning Branch in EPA basically is to identify potential and environmental problems and to try to achieve some sort of study and, if possible, some sort of resolution of those problems before the matter becomes one of general concern and has to be settled in an arena where speed is of the essence, where frequently, rational thought and careful consideration get sacrificed in order for things to be done rapidly.

As part of our attempt to accomplish this, we thought, about 2 years ago, that it might be nice to look at a few industries where people seemed to have the feeling there were a lot of things going on, but nobody really knew what. The idea was to find out exactly what the problems are or if business is just a lot of rumor mongering and in fact, the problems are not nearly as severe as many uninformed people seem to think they are. Accordingly, we set up a series of conferences, which we hope will be a continuing series. We invited people who are knowledgeable, who have things to say, to come to a public forum which would be organized in such a way that all persons, including those not on the program, would have an opportunity to contribute what they could so that we could get a reasonably good picture of exactly what the situation in question is.

Somewhere along the line we abandoned the notion of holding conferences by industries and felt that it would make more sense to do it in terms of a series of processes without necessarily identifying them with industries, even though in many cases the correspondence would be rather close. Consequently, this conference is on printing processes. We hope to discuss any printing operation, regardless of the type of industry to which it is nominally attached.

This is the third conference in the series. I think the series has been successful at what we hoped it to do. These conferences have shown that they can, in fact, stimulate a lot of good discussion and stimulate people to do some thinking about things they might not otherwise have considered.

It is inevitable when you hold a meeting for a general audience that many of the people find some of the matter presented rather elementary while others consider it quite new and interesting. I anticipate that most of you, at one time or another, will feel bored by the presentation on the grounds that you have heard it before. But I also think very strongly that every one of you will find a great number of papers that will in fact tell you things that you did not know before. I certainly hope every one of you goes away from here knowing something you did not know when you came.

I want to make it clear that this is not a witch hunt. This is not an attempt to put the printing industry behind the eight ball. There are no regulatory actions which are expected to stem, in a direct sense, from this conference.

I want to encourage everybody to be open and candid in what they have to say because I think that is the only way we are going to accomplish what we are here to do.

The emphasis in this conference is on the environmental aspects: the external environment, including air and water pollution, waste-disposal problems, and matters of this nature. We realize that it is very difficult if not impossible, to separate the environmental concerns from what you might call microenvironmental concerns, the occupational setting, and some of the papers today will in fact deal with occupational studies. We consider this quite appropriate. However, it is my hope that we do not allow this to turn into a conference on industrial hygiene. The idea of the conference is to discuss the environmental aspects of chemical uses.

Mr. Frank Ayer, who is standing by the door there, is the conference coordinator from Research Triangle Institute. He and his staff are available to help you with your problems. If you have any questions, please seek him out. You will notice he already has grey hair, so you are not going to hurt that too much more.

We are trying something a little bit different on this conference from what we have done in the past. Because this is a general audience and we realize that the industry itself is broken into some rather specialized components, we are going to start with a brief review of practice in printing operations. This review is based on a technical study, which was performed by RTI as a planning step in designing this conference. In the past, we have not presented the results of this study at the conference itself, but we have found that this frequently meant that speakers who really wanted to talk at a technical level had to go back and give a primer to much of the audience about what they had to say. This study, I realize is going to be old news to those of you who are experts in the field, but we hope, by presenting it, to bring some of the nonexpert audience up to a level that will permit the other speakers to launch right into technical material.

OVERVIEW OF PRINTING PROCESSES AND CHEMICALS USED

Ben H. Carpenter and Garland K. Hilliard*

Abstract

This overview of the use of chemicals in the printing industry identifies potentially detrimental effects on the environment or upon health that merit further investigation. The size and diversity of the industry presents a major problem in the study of the environmental aspects of chemical usage therein. As a prerequisite, therefore, the industry is categorized, in logical fashion, into major printing processes, subprocesses, and supporting processes. For these categories, the current status of utilization by the industry as well as the projected status is estimated. Within these categories, different types of printing operations are discussed, along with their products, in terms of the chemical usage and the possibility of air pollution, water contamination, solid waste, and odor generation. The aim is to indicate the scope of potential problems and their relative magnitude within the industry. New inks and processes are reviewed to show their potential roles and impacts on the environment.

INTRODUCTION

The printing industry applies inks, coatings and varnishes, and solvents to papers, textiles, metals, wood, and plastic materials. Press operations themselves involve emissions to the air. Water use is minimal unless water-base inks are used. Supporting processes (composition, photography, and platemaking), however, involve water contamination, including contamination with metallic salts. The amount of solid waste from printing operations varies widely, and depends upon the size of the plant. Both printing operations and supporting processes involve odors to some extent.

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*Ben H. Carpenter, Senior Engineer, Research Triangle Institute, Research Triangle Park, North Carolina; Garland K. Hilliard, Consultant, Engineering Department, North Carolina State University, Raleigh, North Carolina.

Odors arise where chemical solvents are evaporated and where chemically reactive inks are exposed to heat.

Five printing processes have been assessed in a recent survey as sources of organic chemical emissions: lithography, letterpress, gravure, flexography, and screen printing (ref. 1). Heat set inks used in lithography and letterpress generally contain 30 to 40 percent solvents. At least half of this solvent is removed in dryers. Gravure and flexographic inks contain up to 60 percent low-boiling solvent, most of which is removed in drying. The major source of emissions in metal decorating (by lithography and screen printing) is the protective coatings put under and over the ink, rather than the ink itself. Many types of inks and paints are used in screen process printing. This process has the smallest total production of paper substrates, but is applied extensively in textile printing. It is definitely a process to study in terms of pollution and health hazards.

The industry prepares image transfer materials, using photographic typesetting and other processes, from which organic compounds, metallic residues, and scrap can be wasted to the air or to water, or to solids disposition.

PRINTING PROCESSES AND AIR POLLUTION

The status, the products, and the chemical usages of the major printing processes are given in appendix A, which also includes these characteristics of the supporting processes. The pollution potential of each of these operations depends upon the nature of the process employed. Printing operations themselves tend to result in emissions of ink solvents and chemicals, some odor generation, and some solid wastes.

Offset lithography transfers ink from an image area, which is essentially at the same level as the nonimage area. The nonimage area is wet by water and the image area is wet by ink only. Water is transferred to the plate first, followed by the ink.

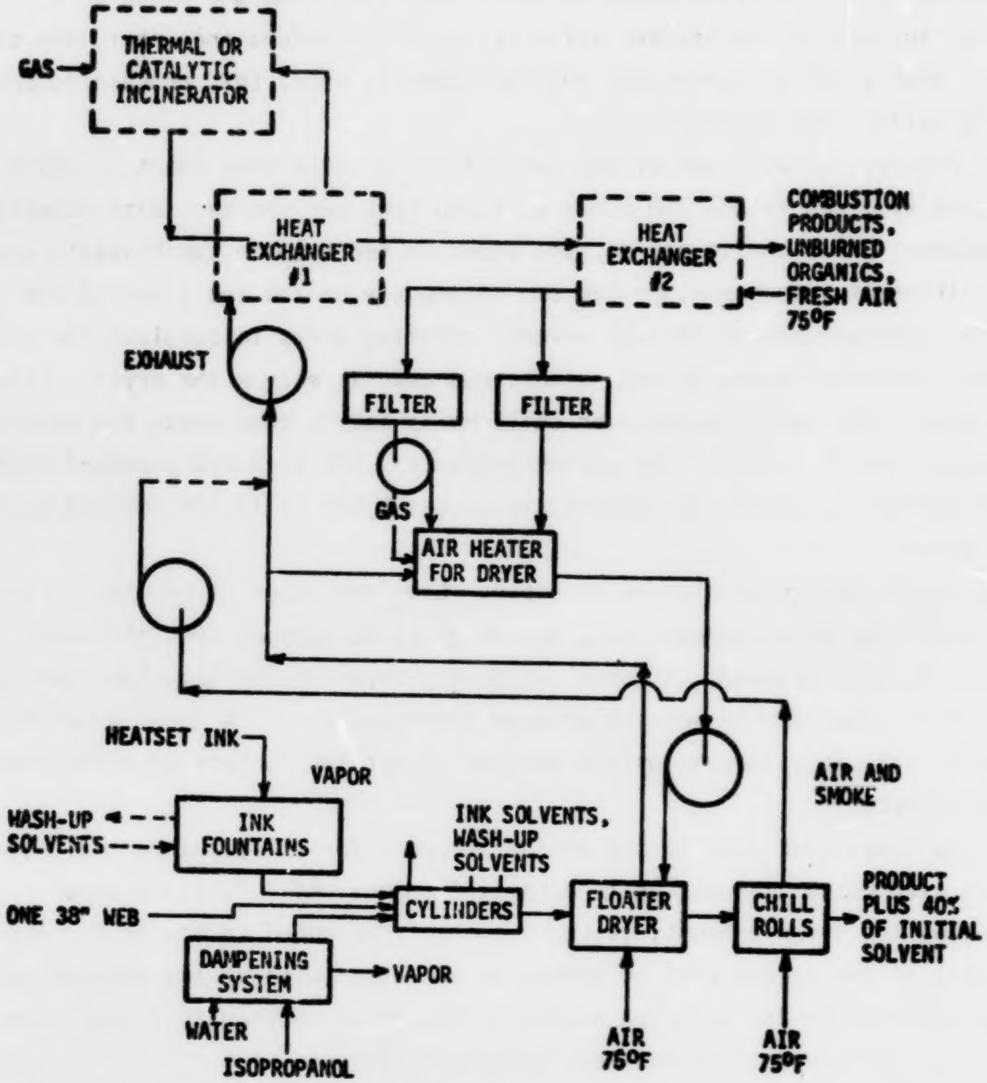
This process customarily employs curved metal plates mounted on a cylinder press. Water used to dampen the plates may contain 15 to 30 percent isopropanol. (If the Dalgren dampening system is used, isopropanol is required.) Ink is transferred to the plate, then from the image to a rubber surface on the blanket cylinder, which transfers the ink to the paper. When a web or continuous roll of paper is used, this process is commonly called "web offset."

Figure 1 shows a web offset publication process flow chart in which a 38-inch wide web enters the press at 1,000 feet per minute. With blanket-to-blanket press configuration, the paper is fed between two blankets and two different images are printed simultaneously on the two sides of the sheet. The web passes through several printing units to complete the printing of complete images on both sides, and then it enters the dryer. Leaving the dryer, the paper passes over chill rolls and is then ready for cutting, folding, and finishing. The system exhausts 1,500 to 3,500 standard cubic feet per minute (scfm) of air; it circulates 6,000 to 10,000 scfm through the dryer.

Other configurations are possible. When the paper is printed on only one side, the dryer exhaust rate may be up to 30 percent less than when both sides are printed. A tunnel (floater) dryer is the only type for use when both sides of the web are printed simultaneously. A steam drum dryer is not applicable because of the problem of wet ink contact with the steam drum surface.

Optional additions to the drying process, for emissions control, are shown with dotted lines. While exhaust from the chill rolls is shown entering the dryer exhaust, it could probably be added to the dryer recycle as part of the makeup air, or simply be exhausted without any correction. More information and data are needed to determine whether chill-roll ventilation air needs treatment to eliminate emissions.

The web offset process, when used to print newspapers and business forms, does not usually employ dryers and air pollution control equipment. Emissions are thought to be low because the inks contain very little solvent, porous paper is generally used, and the coverage is much less with text than with pictorial process color work. The total consumption of ink and its associated solvents in newspaper printing has not been separately tabulated. (Census figures exclude a substantial quantity of captive ink made by large printers for their own use.) Nor is there much data on actual emissions.


GAS
THERMAL OR CATALYTIC INCINERATOR
HEAT EXCHANGER #1
HEAT EXCHANGER #2
COMBUSTION PRODUCTS, UNBURNED ORGANICS,
FRESH AIR 75°F
EXHAUST
FILTER
FILTER
GAS
AIR HEATER FOR DRYER
HEATSET INK
VAPOR
WASH-UP SOLVENTS
INK FOUNTAINS
INK SOLVENTS, WASH-UP SOLVENTS
AIR AND SMOKE
ONE 38" WEB
CYLINDERS
FLOATER DRYER
CHILL ROLLS
PRODUCT PLUS 40% OF INITIAL SOLVENT
DAMPENING SYSTEM
VAPOR
WATER
ISOPROPANOL
AIR 75°F
AIR 75°F

(Optional equipment shown dotted; letterpress and offset incineration systems are interchangeable.)

Figure 1. Web offset publication.

Sheetfed lithography uses either coated or uncoated paper, and applies low solvent, oxidative-drying inks. Isopropanol is commonly used in fountain solutions. Ink usage is much less than in web offset publication because of the lower feed rate and also because usually only one side is printed.

Letterpress printing transfers ink directly to the paper from the image surface, which is raised slightly above the rest of the plate.

In letterpress newspaper printing, the image is transferred to a mat which can be curved to make a cylinder plate. No dampening solution is used in this process. Washup solvents are, however, used on the press. All other air and organic emissions are from the dryer unless an incinerator is used, in which case the only exhaust is from the incinerator. In a few cases, a catalytic incinerator has been installed in a recycle line for the dryer. This has not necessarily eliminated the need for another incinerator for the exhaust gases.

Letterpress newspaper printing tends to emit relatively inert ink mist and paper dust. The amounts are claimed to be noticeable only in very large installations and can presumably be controlled by an air conditioning system; that is, by moderate filtration of the air. Filters are sometimes placed in ducts located over the presses to remove some of the ink mist and paper dust.

Letterpress publication printing uses different inks for color reproduction, etc. Also, different papers are used, and the inks are not dried by absorption alone. These differences lead to different problems in emission control.

Sheetfed letterpresses tend to use more ink than sheetfed offset presses, because the letterpress ink film is two to three times as thick as the lithographic ink film.

Metal decorating processes transfer the image by lithography or screen to a dried (usually vinyl) lacquer undercoat applied to the metal sheets. Several colors may be applied. After printing, a trailer roller coater puts a varnish coating over the wet ink, and the sheet is dried again. For bottle caps, a thick coating of varnish is put on the outer side and dried. Sheets leaving the 300° F drying ovens may still have 7 to 10 percent solvents (ref. 2). Coating thickness and solvent content influence the percent solvent in the oven exhaust. Exhaust rates are usually set to limit solvents from 10 to 25 percent of the lower explosive limit. Since the inks themselves contain little solvent, the emissions from lithographic metal decorating are small compared to those from coating application and drying. Solvent is not always exhausted from the roller coating area.

Flexography, like letterpress, transfers ink directly from the plate to the paper or substrate. The plate image area is raised above the rest of the surface. It is made of rubber, however, and alcohol-base inks are used; these characterize the process as flexography. Most flexographic inks contain about 55 percent organic solvent. There are, however, three types of inks: solvent inks, steam set inks, and water-base inks. When solvent inks are used, the product may be steam drum dried or air dried at 140° F, and then passed over chill rolls. It is assumed that more solvent is driven out in the dryer than at the inking area, but the ratio is not known. About 90 percent of the applied solvent is believed to be driven out during and after printing. The remaining 10 percent of the original solvent would evaporate slowly from the solidified vehicle resins on the cool web.

Steam set inks, employed in the "water flexo" or "steam set flexo" process, are low-volatility inks of a paste consistency, which are gelled by water or steam. The vehicles generally consist of a glycol type solvent almost saturated with a resin. The addition of water lessens the solvent power of the glycol, causing the resin to precipitate and gel the vehicle. Further gelling occurs as the solvent penetrates the substrate. This process is used for paper bag printing. No significant emissions have been observed from this process.

Water-base inks are based on aniline dyes, but are now usually pigmented suspensions in water. A dryer is often employed, but since the solvent is water, no emission problems arise.

Gravure processes employ an image recessed relative to the surface of the image carrier. Ink is transferred directly from the image carrier to the paper, film, or other substrate. Since the ink is picked up in the image area and the excess scraped off the nonimage area with a doctor blade, its viscosity is kept low by a relatively large amount of low-boiling solvent. Control of solvent vapors around the ink fountain is necessary to avoid explosions.

Gravure may be sheetfed or roll fed (rotogravure). Rotogravure is used for coated or uncoated paper, film, foil, and combinations thereof. The process employs either steam or hot air drying at 90° to 150° F. Solvent vapor control is used at the press, the dryer, and the chill rolls. Activated carbon can be used to absorb the vapors, since there are no combustion products or solvent breakdown products in the exhaust. The concentration of solvent in the exhaust from the activated carbon beds is not known, and reliable data are not available.

U.S. plants have recently begun to apply heat-transfer printing to textiles, using the gravure process. The desired pattern is applied to dry-transfer paper, and heated to volatize it onto the fabric. Current production is some 40 million yards of dry-transfer paper (ref. 9).

Screen printing employs a fine screen for the image area, through which ink or paint can be forced. Nonimage areas are produced by coating the screen to mask off the ink. The amount of organics exhausted into the air depends on the type of ink used. When water colors (for posters), or water-base emulsions (fabric printing) are used, there are no significant emissions. This is also the case if oleoresinous poster inks or alkyd enamels are used. Fast-drying lacquer inks cause significant emissions, however. Evaporation takes place in the printer and the dryer. No information about the percent solvent removed in each operation is available. It is predicted that the solvent will continue to evaporate on the drying racks, although the ink may dry enough to overprint. A study on solvent retention in poly (methyl methacrylate) films--not inks--shows 6 percent residual toluene solvent after 6 months air drying (ref. 3).

Flat and rotary screen printing processes are used to print textiles. Resin-bonded pigments are frequently used (ref. 8).

Thermography is an extension of the printing process, in which the image is raised on a printed page to give the effect of engraving. Either resinous powders are deposited on the print or specially formulated inks that swell on heating are used. Only a few manufacturers who specialize in business or social stationery practice this process.

There are five basic steps, if inks and powder are applied separately. The form is printed as usual by letterpress, or lithography, each having its own characteristic losses of solvents to the air. A raising powder is applied to the printed sheets so that it adheres to the wet ink. Excess powder is removed from the remainder of the sheet. The entire sheet is heated so that the powder melts and fuses with the ink. The sheet is cooled, causing the molten powder to harden. The powdered resins are a potential air pollutant, in their recovery and recycle. Where inks contain the powder, premixed, the process requires only two steps, printing and heating. There is less danger of pollution.

SUPPORTING PROCESSES AND WATER POLLUTION

In addition to the printing processes themselves, there are certain associated processes which are a part of the industry: binding, composition, photography, and platemaking. These appear to generate few problems of air pollution, but are sources of water pollution.

Binding involves the application of hot glues to books, magazines, and commercial forms. Unless solvents are used, the emissions are mostly water vapor. Spiral binding involves the attachment of a plastic binder to specially punched text material. Dusts and waste paper are the principal potential pollutants; chemicals are not involved.

Composition is that step in which the "layout" or model of the copy is converted to press-usable form, either by the hot type method or the cold type method (see appendix A). The hot type method does not employ chemicals. It is used mostly for letterpress printing. In linotype and monotype operations, water may be used for noncontact cooling although most of the machines are air-cooled. Average usage would be about 11,000 liters/day per machine, and a large newspaper would require 20 to 25 linotypes (ref. 10).

Cold type composition includes photo composing, where water is used in the developing and fixing of the output from the typesetting machine. Waste characteristics are similar to the photographic processing wastes to be discussed next. Volumes are generally low, about 5,700 liters/day for one machine, which is adequate for all but the largest printing operations.

Photography is employed (essentially in all the basic printing processes) in the development of film for printmaking and in the development of black and white prints in cold type processes. Organic vapors are emitted from developing baths and dryers. Wash and rinse waters from automatic film developers, and from tray developers, have been sampled and tested for contamination (ref. 10). For the rinse waters, chemical oxygen demand (COD) ranged from 100 to 310 milligrams per liter (mg/l), aluminum from 2.5 to 7 mg/l, and silver from 0.6 to 5.5 mg/l.

These wastes were toxic to unacclimated seed, and therefore no data on biological oxygen demand were obtained. Other studies have shown that these wastes are amenable to treatment in acclimated biological waste treatment systems (ref. 11).

Photographic solution wastewaters showed COD's of up to 64,000, aluminum up to 1,300 mg/l, and silver to 3,400 mg/l before recovery.

In platemaking, potential for pollution varies with the printing process involved. Flat-bed letterpress plate preparation does not use water, nor are there solvent emissions to air in the simple assembly of type with "half-tones," that is, engravings usually made in an engraver's shop.

Cylinder letterpress plate preparation requires water for prerinsing, etching, and postetching rinses. The chemicals used depend upon the type of plate. Magnesium plates are most commonly used. Zinc and aluminum are alternatives. Prerinse solutions containing nitric acid, gum arabic, and water prepare the plates for etching. About 0.5 liter is used per plate. The wasted solutions have shown up to 31,000 mg/l COD, 49 mg/l aluminum, 0.26 mg/l chromium, and 18 mg/l zinc (ref. 10).

During the etching step, about 200 grams of magnesium are dissolved from each plate, using a solution containing nitric acid, detergents, surfactants, and water-soluble solvent. Wastewaters from aluminum plate etching have shown up to 27,000 mg/l magnesium, 1,400 mg/l aluminum, and 430 mg/l zinc. Where aluminum or zinc plates are etched, wastes have shown 23,000 mg/l aluminum and 56,000 mg/l zinc, respectively.

Postetch rinses use about 6 to 10 liters of plain water per plate. Grab samples have shown COD values to 3,100 mg/l, to 6 mg/l aluminum, to 140 mg/l magnesium, and to 2.9 mg/l zinc.

Flexography plates are etched with caustic. No sample data are available; however, large platemakers are reported to use only about 95 liters of solution per week.

Offset plates for lithographic printing are rinsed free of developers. Manual rinses require about 30 liters per plate. Automatic rinses use more water, and usage is proportional to plate length (up to 176 liters for a 140-cm-long plate). A typical large shop might process 35 plates per day. The rinse waters have shown COD's up to 2,000 mg/l, and total suspended solids of up to 100 mg/l.

Rotagravure plates (cylinders) are first washed with acetic acid, then treated with nickel salt solutions, rinsed, and plated with a thin film of copper. The plating solution is replenished but seldom discharged. After plating, the cylinders are rinsed with about 30 liters of water. One plant's waste shows up to 620 mg/l copper and up to 1.2 mg/l aluminum (ref. 10). The plated cylinder is wet polished, and the effluent waters have shown to 90 mg/l suspended copper. The polished surfaces are etched with concentrated ferric chloride, which is either used to depletion or replenished. The etched surfaces are rinsed to remove dissolved metals. The rolls are finally subjected to developing and cleansing washes requiring about 700 liters of water per cylinder. The chemicals used are usually sulfamic acid, methanol, and diacetone alcohol. Postetched rinse wastes show up to 5,400 mg/l iron, up to 600 mg/l copper, and up to 290 mg/l suspended solids.

SOLID WASTES AND ODORS

The amount of solid waste from printing operations varies widely, and depends upon the size of the plant. Large plants spoil about 3 percent of their paper, while smaller plants spoil much more (ref. 12). Most paper scrap is baled for sale. Metal scrap is nearly all recycled. Silver is usually recovered from photography wastewaters. Most of the problems of solid wastes and their chemicals arise in the recycling and disposal industries, not in the printing operations themselves.

Since paper is recycled, treatment processes are applied to remove the inks. Detergents are used, and salts are added to differentially precipitate the cellulose and ink particles suspended in water (ref. 13).

Peroxides have been proposed for removal of printing inks (ref. 14). The feasibility of feeding waste paper to farm animals as a source of cellulose has been explored. The presence of polychlorinated biphenyls makes the practice questionable (ref. 15).

Photographic developers and wash solutions usually contain odorous volatile solvents. The odor of acetic acid is often present in photography process areas. This acid has been shown to be harmful to workers' eyes, and is usually removed from the work area with exhaust fans. It is doubtful that the resulting concentrations in the ambient air would have a detectable odor.

Some inks produce odors as the result of chemical reaction during the printing or drying operations, and others, by interaction with the substrate. Most of the odors from inks, however, are those of the solvents employed. No crucial odor problems have been identified at this time.

TYPES OF CHEMICALS USED

A complete listing of the chemicals employed in printing processes would be endless, even if it were possible.* Much of the formulations utilized are bought by the printers from manufacturers who sell under trade names and guarantee performance. The compositions of their formulations are not disclosed. This itself is a problem in the search for potential hazards needing controls and standards. The drying operations employed in printing can decompose certain solvents contained in the inks, so that emissions are not the same compounds as those fed to the system. The extent to which such decompositions occur is known to be influenced by the kind and quality of paper, textile, or other substrate employed.

At the present time, the restrictions imposed on hydrocarbon emissions from stationary sources are expected to affect the printing industry extensively because their chemicals yield these types of emissions. Sulfur oxides and carbon monoxide are not problems. Solid particulates do not generally present problems, but plume opacity will be a problem. Nitrogen oxides may present problems where noncatalytic incineration is employed.

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*A partial listing is given in appendix C.

The modification of materials has been rapid and extensive in the last several years so that many printers may have choices of inks and other materials which can effectively control, or at least help control, their pollution problems.

INKS

Letterpress inks are viscous pastes. Vehicles used are slow-drying alkyds or vegetable oil (e.g., linseed oil) derivatives. These inks dry by oxidation and polymerization, during which chemical changes occur that can result in odorous products. Oxidation may be promoted by the addition of reactive ingredients, and these may be volatile or may cause odors. Polymerization may be catalyzed by certain metal salts of organic acids. Although these inks do not dry for several hours, they set (with the assistance of spray powders to protect the printed film) sufficiently to allow satisfactory overprinting through successive units, such as in multicolor work. They are not acceptable, however, for high-speed web operations in letterpress and in offset. These require an ink that will dry in a second or less. Heat-set inks were developed to fill this need. They contain varnishes made by solubilizing solid resins in high-boiling hydrocarbon solvents. A typical heat-set ink may contain 35 to 45 percent of petroleum hydrocarbons with a boiling range of 450° to 550° F. The inks are dried by rapidly removing the solvent as the paper web passes through a drier at temperatures as high as 400° to 500° F. Some thermal degradation, principally of ink and paper components, does occur.

Ink manufacturers have sought a more economical means of printing with high-speed processes than putting solvent into an ink before printing and promptly removing it immediately thereafter. New inks that represent technological advancement beyond solvent reformulation include thermally catalyzed single- and two-component (heat-reactive) systems and ultraviolet-sensitive (photoreactive) systems. These have progressed to commercial feasibility in the United States. Thermally-catalyzed inks contain a prepolymer, a cross-linking resin, and a catalyst. The catalyst activates at 350° F in the drier and converts the liquid into a solid polymeric film via condensation polymerization reactions. Reaction byproducts are principally

C_1 -C_4 alcohols, moisture, and small amounts of formaldehyde; thus, condensate buildup is prevented in the drier. Overall volatile content of such inks is 20 percent or less of that of the conventional heat-set inks. The smoking tendency is practically nil. Stack odor is said to be reduced (refs. 17,18,19).

Because heat is required for drying, these inks cannot be used on sheetfed presses. The inks have objectionable inplant odors. They are at this time expensive (35-80 percent more than heat-set). They are reported to permit buildup of static electricity in the folding operation. More information is needed concerning the extent of applicability and acceptance of this product.

Photoreactive ink systems (UV-inks) consist minimally of one or more monomers and a photosensitizer that selectively absorbs energy. No solvents are contained in the mixture. There are no byproducts since the reaction is addition polymerization. The paper is not heated above 50° C, and a minimum of moisture is lost in the process. The inks do not react until exposed to ultraviolet light; they therefore may be allowed to remain in the fountains and on the rollers for long periods of time. These inks offer advantages to sheetfed lithography; eliminate "set-off," the unintentional transfer of ink to adjacent sheets before the ink has dried completely; eliminate use of powders that are applied to protect an ink film that is "set" but not "dry"; and eliminate the storage of printed sheets for ventilation, required in oxidative drying processes. Disadvantages of this system include cost (75-100 percent more expensive than conventional heat-set inks), the use of expensive UV lamp systems, hazards of UV-radiation to operating personnel, and the formation of ozone by the action of ultraviolet light on oxygen. Conventional commercial procedures will not deink papers printed by this process. This process is, however, at present in commercial use, and more information is required concerning progress in its implementation.

Inks used in lithography are similar to those used in letterpress. Flexography, however, uses inks of low viscosity, made of solvent-resin systems colored either with dyes, pigments, or combinations thereof. The film-forming ingredients vary but usually are soluble in alcohol, alcohol-hydrocarbons, or water. These inks are often employed in metal decorating.

Some of them, when permitted to come in contact with metals, undergo a chemical reaction and yield a marked odor which is offensive in products, but is not a pollution problem.

Rotogravure inks are low-viscosity solutions of resins in suitable solvents. Air drying presents potential pollution problems. Among the conventional solvents used, toluene and xylene have appreciable odor. To some extent the solvents have been replaced with alcohols having a much milder and less objectionable odor.

Screen printing inks contain a variety of solvents, adhesives, water colors, and emulsifiers. Fast-drying lacquer inks are a serious source of pollution. Among new approaches to pollution control is the use of microwave drying, which tends to evaporate polar solvents without degradation. This technique is indicated for use in gravure and flexography and offers a means of using extensively water-base gravure on plastic substrates. Metal substrates present a problem because they reflect microwaves back to the applicator and damage it. Microwaves are a potential health hazard should leakage occur. Commercial trials in Europe with microwave units for drying inks on cartons have been sufficiently successful that several large European companies reportedly have installed such dryers (ref. 20). The general acceptance of this system is a long time away.

Radio frequency drying is under experimental development. Electron beam drying offers the potential for elimination of solvents and catalytic agents in the inks, but has the disadvantages of degrading the paper under the heavy dosage required, and of generating X-rays, thus necessitating elaborate and expensive operator protection.

The following companies have introduced heat-reactive and/or photoreactive inks: Bowers Printing Ink Company; Kohl and Madden Printing Ink Corporation; Richardson Ink Company; Roberts and Porter, Inc.; Sinclair and Ballentine; and General Printing Ink Division of Sun Chemical Corporation. Three companies have advanced to the stage of press trials with ultraviolet ink: Sinclair and Ballentine, Jensen Printing (a subsidiary of Holden Industries, Minneapolis), and I. S. Berlin in Chicago.

Further information needs to be brought forth at this time concerning solventless inks. The Lithium Corporation of America introduced in 1971 a new liquid, polybutadiene-alphamethylstyrene copolymer resin for solvent-free manufacture of printing inks. Trademarked Lithene-Y, the resin series, which was to be available in high and low molecular weights, eliminates the need for solvents because of the low viscosity of the 100-percent reactive materials. The Richardson Ink Company recently introduced its "Duralum Mark V Ink," which should eliminate the need for overprint lacquer when printing aluminum beverage cans. Further information concerning this product would be desirable.

In recent years, there has been a tendency towards increased use of pigments in textile printing. Pigments are molecular aggregates, insoluble in the media to which they are subjected during application and use. They may belong to any chemical class of colors, but they do not contain groups capable of interaction with fibers. Their fixation is achieved, therefore, with the use of a binder which encloses them and provides a bond between them and the fiber. The binders are high-molecular-weight, film-forming materials produced by polymerization of simple intermediates that are initially present in the printing paste. After evaporation of solvent, a thin coherent coating is produced by heating. This film encloses the pigment particles and adheres to the fiber. The rubbing, washing, and drycleaning fastness properties of a pigment print are, therefore, those of the binder film. The most important monomers in modern binders are derivatives of acrylic acid, butadiene, and vinyl acetate. To some extent, urea, melamine, and related products are significant as raw materials for the manufacture of formaldehyde condensates suitable as binders. In pigment printing, white spirit emulsions employed for thickening cause several problems: flammability, odor, and air and water pollution. There is a need for reports of development work underway to reduce or eliminate these problems. The recent development of fully synthetic water-soluble thickeners has enabled the first step to be taken toward avoidance of white spirit. These thickeners are polyacids of very high molecular weight attained by special processes and supplied in various formulations. Their common feature is their unusually high specific thickening action after neutralization.

Wastewaters from printing operations have been shown to contain varying if not high amounts of metals, total suspended solids, and materials contributing to chemical oxygen demand. Because of this, the extent of effluent reduction attainable through application of the best available technology has been estimated (ref. 10). For example, rotagravure monthly average limitations for effluents have been projected as follows: aluminum, 0.5; COD 5, 30; chromium, 0.5; hexavalent chromium, 0.05; copper, 0.5; pH, 6-9; silver, 0.05; total iron, 1; total suspended solids, 30. All units are grams per cylinder except for pH, which is in conventional units for this determination. More information is needed concerning the application of treatment technology and the extent to which these recommended standards can be met. Costs of complying with these standards also needs to be projected at this time.

SUMMARY AND RECOMMENDATIONS

This review of chemical usage in the printing industry shows the industry to be a dynamic and varied enterprise now going through an era of substantial change, part of which has been motivated by the needs for pollution control and for protection of worker health. The letterpress process now has approximately 35 percent of the market which it supplies and is growing at a rate of about 2-1/2 percent per year. Lithographic processes, however, are enjoying a 12 percent per year annual growth. Flexography is predicted to grow in newspaper and publishing areas. It will be adapted to letterpress and offset processes in the near future. Gravure has about 8 percent of the printing market and it is predicted to capture up to 11 percent in the 1980's. Its growth is about 10 to 12 percent a year. It is concentrated in a few highly specialized plants. The screen process now has 2 percent of the total printing market; it is not expected to grow substantially except in the printing of fabrics, textiles, and carpets. It is definitely, however, a process to study in terms of pollution and health hazards. Composition, photography, and platemaking aspects of the industry are undergoing rapid changes, some of which direct toward more air pollution and less water pollution.

Many of the solvents utilized in this industry are hydrocarbon in nature, and amenably to control by incineration, absorption, and other conventional processes. Industry is, however, beginning to be in the position of having a choice between the old solvent-base inks and materials and the new nonsolvent-base inks employing different processes. Some of the new processes available for use with solventless inks involve new hazards which require some study and evaluation. In this connection, textile printing, with its vast variety of pigments, dyes, colors, and inks, and its extensive list of proprietary formulations, is almost a special category itself.

In view of the extensive innovations carried on in recent years, it is recommended that a conference at this time concentrate on the clarification of the findings of these innovations, on the extent of commercialization of any processes or procedures that tend to alleviate pollution problems, and on thoroughly delineating through discussion involving experts the advantages and disadvantages of the approaches. The industry should be reviewed at this time in terms of its future and current trends. The program participants must, if this recommendation is adopted, include personnel of companies supplying materials--inks, papers, other substrates--and equipment peculiar to the industry. Less factual information is available concerning air pollution than concerning water pollution, primarily because more extensive sampling and testing has been performed on wastewater samples. It is recommended that part of the sessions of the conference focus upon new measurements of the effluents and emissions from printing processes.

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APPENDIX A
PRINTING PROCESSES, PRODUCTS, AND CHEMICAL USAGE

Process	Status	Products	Chemicals
1. Letterpress (relief printing)	35% of market; Ave. annual growth 1963-72: 2.5% (5)	Gold stamping Die cutting Forms Stationery Pamphlets, brochures Books	Inks - Dry by absorption, chemical oxidation, and evaporation. Driers Cobalt
A. Sheet-Fed Press Types { Platen Cylinder Composition: Handset Machine Linotype Ludlow Line-casters		Magazines Newspapers Tags Labels 4-color process NCR forms*	Varnishes Reducers Retarders (nonskin) Type wash* Press and roller wash* Spray powders Flame dryers
B. Web-Fed Print from: Stereotyping Electrotyping Photogelatin plates		Newspapers Books Magazines Continuous forms Snap-apart forms	News inks Dry by absorption Process inks Dryers Varnishes Reducers Retarders Type wash Press and roller wash Spray powders (to prevent setoff) Flame dryers
2. Flexography (relief printing) Print from rubber or photopolymer plates. Bakelite plates	Predicted to grow in newspaper and publishing industry. (1) Will be adapted to letterpress and offset processes in future.	Plastic film Foil bags Milk cartons Cardboard cartons Gummed tape Bread and candy wrappers Newspapers and magazines on increase	Water-base catalyzed inks Ultraviolet inks
3. Lithography (Planography)	55% of market Ave. annual growth 1963-72 = 10.2% (5)		Platemaking Sensitizer coatings Desensitizers Developers (lacquers) Gum arabic
A. Sheet-Fed	92% of litho commercial printing in the next 5 years. (6) Presently growing at rate of 6-8% per year. (7)	Small newspapers Greeting cards Maps Posters Labels, tags NCR papers Forms Stationery Brochures, booklets Magazines Books	(preservative) Image removers Subtractive developers for subtractive plates Plate cleaner (to remove toning)* Carbon arc (can exceed ozone limits established by OSHA) Mercury lamps

Newspaper industry - largest single industry in terms of $ - predicted $10.8 billion in 1975.

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*Identifies possible toxic materials.

APPENDIX A (con.)

Process	Status	Products	Chemicals
3. Lithography (Planography)			
A. Sheet-Fed (con.)			Plate materials Aluminum - 95% of all;* Zinc; Brass; Copper; Chrome plate; Steel Pressroom Gum arabic Fountain solutions to maintain pH 1) glycerine and 2) alcohol Powder spray dryers to prevent offset Flame dryers to set ink Roller and blanket wash Rubber rejuvenator Inks Reducers*, varnishes*, driers* Retarders (to prevent "skin")* Fluorescent inks* Metallic inks Regular inks* Plastic ink Foil ink
B. Web-Fed	Presently growing at 10-12% per year. (7) Will amount to 8% of total litho commercial printing in next 5 years. (6) Faster growth rate, but is starting from a smaller base.	Newspapers Magazines Books Foils Plastics Metal decorating Continuous forms Snap-apart forms	Pressroom Same as sheet-fed Inks Process inks Ultraviolet (UV) inks Heat-reactive inks
4. Gravure (Intaglio)	8% of printing market. Predicted to capture 11% in 1980's. Fastest growth rate of 10-12% per year. (5)		Platemaking Etches (25% nitric acid) Fixers Developers
A. Copperplate and steelplate	Highly concentrated in few highly specialized plants.	Announcements Invitations Social stationery Business stationery Government currency Government bonds Postage stamps	
B. Photogravure	Slow and expensive, limited use. Mostly done by hand.	Fine paintings Photographs	Plates Prepared photographically and etched chemically.
C. Rotogravure Printing done by rotary presses. Paper fed from rolls (web) ink in liquid form.	Most predominant of gravure processes. Fastest growth rate of all printing processes of 12-15% per year. (7)	Catalogs Magazines Wallpaper Fabrics 17% specialty printing(4) 27% packaging 50% publications	Cylindermaking Semiauto gravure cylinder etching machines Electronic color scanners

*Identifies possible toxic materials.

APPENDIX A (con.)

Process	Status	Products	Chemicals
4. Gravure (Intaglio)			
C. Rotogravure (con.)		Wood grain coverings Vinyl sheeting Decorative high-pressure laminates Foil	Electronic gravure cylinder engraving Pressroom Electronic ink transfer process Inks
For more information: Gravure Research Institute Gravure Technical Association			
5. Screen-Process	2% of total printing market. (5) Not expected to grow substantially. Definitely a process to study in terms of pollution and health hazards.	Posters Billboards Glass bottles and jars Book covers and ribs Toys Furniture Fabrics Oilcloths Glass plate Felt banners Printing circuits Dials Metal Clay	Screenmaking Pressroom (solvents, sprays, etc.) Lacquer thinners Mineral spirits Reducers Inks Oil paints, enamels, poster paints, lacquers, varnishes, vinyl (fusion),* metallic, plastic inks, adhesives Washup and cleaning
6. Thermography A process used to raise the image on a printed page after being printed by letterpress or litho process. Gives the effect of engraving. Process uses either a resinous powder which is deposited on ink after printing or specially formulated inks that react to heat causing ink to expand or "swell" thus raising the image from the paper.	Process performed by relatively few manufacturers who specialize in social and business stationery.	Announcements Invitations Social and business stationery	Inks Resinous powders, e.g., embossograph Hi-Flo neutral powder Formulated inks Flourescent powders
7. Binding			
A. Bookbinding			Hot glues
B. Magazine binding			Hot glues

* Identifies possible toxic materials.

APPENDIX A (con.)

Process	Status	Products	Chemicals
7. Binding (con.)			
C. Forms padding			Padding cements
D. Spiral binding			
8. Composition			
A. Hot type	Used primarily for letterpress printing.		
1. Hand composition	Individual characters set up in composing stick; characters already formed; used primarily for large display lines.	Lines of type made up of individual characters.	No chemicals
2. Monotype	Individual characters cast on machine.	Lines of type made up of individual characters.	Lead
3. Linotype	Whole line of characters cast on machine	Lines of type characters cast together.	
4. Ludlow	Individual characters strip rule, and spacing material cast.	Lines of type characters cast together.	
B. Cold type	Used primarily for lithographic printing process; also used in gravure, silk screen and letterpress.		
1. Copy-producing typewriters	Used in smaller plants for copy preparation.	Paper copy	None
Brands { Varityper Justowriter IBM Lithotype			
2. Photocomposing machines Intertype fotosetter ATF photo compositor Computer composition	Used in large plants, newspapers, publications, etc.	Sensitized films on which characters have been photographed.	Developers Fixers Stop baths Hardeners
9. Photography	Most extensive use in litho process. Also used in other printing processes to reproduce drawings, illustrations, photographs, complex ruled forms, 4-color process. Large portion of photography done in trade shops that specialize in photography for printing industry.	Negatives and positives	Films Developers Fixers

APPENDIX A (con.)

Process	Status	Products	Chemicals
10. Platemaking			
A. Lithographic plates	Covered under litho process. Both sheet and web.	Aluminum or bimetal plates	
B. Photoengraving			
1. Letterpress	A photographic process on sensitized thick metal plates. Used in sheet-fed letterpress process.	Relief engravings of photographs (color and black and white) illustrations. Complex forms.	High-intensity light Carbon-arc Infrared light Mercury Nitric acid Fixers
2. Gravure	Also covered under gravure process	Intaglio engravings of everything produced by gravure process.	Essentially same as above
C. Electronic gravure cylinder engraving	Used in rotogravure	Intaglio engraved cylinders.	
D. Stereotyping To convert flat printing surface to curved printing surface.	Used primarily in newspapers where duplicate plates are needed in high-speed web letterpress operations. Declining use.	Curved plates with relief images.	Lead
E. Electrotyping	Used primarily in publications industry where duplicate plates are needed in web-letterpress operations. Declining use. Very specialized--not usually found in printing plant.	Same as stereotyping (above) but gives finer detail and more durable.	Chrome, Copper, Nickel } Deposited by electrochemical action Lead bases Wax
F. Rubber plates	Used extensively in flexography, but also in letterpress.	Rubber plates	Bakelite plastic Sensitizers Etch (caustic) Rinse (water) Rubber powders
G. Photopolymer plates	Used in web-letterpress processes, primarily publications industry.		
H. Screens	Used in screen print process. Covered under screen printing.		

APPENDIX B
LIST OF ASSOCIATIONS TO BE CONSIDERED FOR PRINTING CONFERENCE

Academy of Screen Printing Technology
Acme Printing Ink Company
Advertising Typographers Association of America
Alden Press Inc. (John Blair & Co.)
Alling & Cary Company
Amalgamated Printers' Association
Ambassador College Chemistry Dept.
American Can Company Env. Services
American Color Print Society
American Dyestuff Reporter
American Education Publications (Xerox Family Education Services)
American Photoplatemakers Association
American Printed Fabrics Council
Anchor Chemical Co., Inc.
ANPA Research Institute
Association of College and University Printers
Association of Flock Processors, Inc.

Baird-Ward Printing Co., Inc.
George Banta Co., Inc.
Basic Controls Systems, Inc.
Binding Industries of America
Bowers Printing Ink Company
Braden-Sutpkin Ink Company
Brown & Bigelow
Bruce Offset Company
Burd & Fletcher Company

C & I Girdler, Inc.
Cadillac Printing & Lithographing
Canada Printing Ink Co., Ltd.
Canadian Lithographers' Association
Canadian Printing Ink Manufacturers' Association
Capitol Printing Ink Co.
Case-Hoyt Corporation
Champion International
Chicago Department of Environmental Control
Chilton Printing Company
Cities Service Oil Company
J. L. Clark Manufacturing Company
Colwell Press Inc.
Commercial Ink Industries
Consolidated Education Publications Inc.
Continental Can Company
Converters Ink Company
Courier Citizen Company
Consolidated Printing Ink Company
Creative Printers of America, Inc.

DeLuxe Check Printers, Inc.
A. B. Dick Company
R. R. Donnelly & Sons
Dow Chemical Company
E. I. duPont deNemours & Co., Inc.

Eastman Kodak Company
Egyptian Lacquer Manufacturing Co.
EPA National Field Investigation Center

Fawcett Printing Corporation
Flexographic Technical Association
Flint Ink Company
Foote & Davis

GATF Air Pollution Control Advisory Commission
General Foods Corporation
General Motors Photographic
Goudy Society
Granco Equipment Inc.
Graphic Arts Advertisers Council
Graphic Arts Association Executives
Graphic Arts Industries Association
Graphic Arts International Union
Graphic Arts Technical Foundation
Graphic Communications Computer Association
Gravure Research Institute
Gravure Technical Association

H-C Industries Inc.
W. F. Hall Printing Company
Hallmark Cards, Inc.
Harris Intertype Corporation
Harris-Seybold Company
Heeken Can Company
Herbick & Held Printing Company
Hercules, Inc.
Hirt Combustion Engineers
Hurletron Inc.

Illinois EPA, Naval Armory
In-Plant Printing Management Assn.
Inland Steel Container Company
Inmont Corporation
International Association of Printing House Craftsmen
International Association of Siderographers
International Business Forms Industries
International Paper Company
International Plate Makers, Die Stampers' and Engravers' Union of North America
International Press Institute
International Printers Supply Salesmen's Guild
International Printing and Graphic Communications Union
International Printing Pressmen's Union of North America
International Repro Graphic Blueprint Association
International Typographic Composition Association, Inc.
International Typographical Union

Kable Printing Company
Kimberly-Clark
Kingsport Press, Inc.
W. A. Krueger Company

Lassen & Jones
Los Angeles County Air Pollution Control District

McCall Printing Company
Machine Printers and Engravers Association

M G D Graphic Systems
Magie Brothers Oil Company
Charles T. Main
Master Textile Printers Association
Meredith Printing Company
Mid-Atlantic Graphic Arts Review
Miller Printing Machine Company
Minnesota Mining & Manufacturing Co.
Mobil Chemical Company
Southam Murray
National Association of Grained Plate Manufacturers
National Association of Litho Clubs

National Association of Printers and Lithographers, Inc.
National Association of Printing Ink Manufacturers
National Composition Association
National Metal Decorators Association, Inc.
National Printing Equipment Association, Inc.
National Printing Ink Research Institute
National Publishing Company
New York News

Ohio Art Company

Parker Metal Decorating Company
Perry Printing Company, Inc.
Photopress Inc.
Platemakers Educational & Research Institute
Pollution Control Industries, Inc.
Post Card Manufacturers Association
Prairie Print Makers
Print Advertising Association
Print Council of America
Printing Estimators and Production Men's Club
Printing Industries of America
Printing Industry of Illinois Association
Printing Platemakers Association, Inc.

Rand McNally & Company

Readers Digest Association, Inc.
Regensteiner Publishing Enterprises, Inc.
Research and Engineering Council of the Graphic Arts Industry, Inc.
Richardson Company
Riverside Press
Roberts & Porter, Inc.
Ross Engineering

St. Regis Paper Company
Salesmen's Assn. of the Textile Dyeing and Printing Industry
Screen Printing Association International
Shell Chemical Company
Sherwin-Williams Company
Silk and Rayon Printers & Dyers Association
Simplicity Patterns Co., Inc.
Standard Gravure
Standard Publishing
Steck-Warlick Company
Sun Chemical Company
Sunnyside Products Company

TEC Systems, Inc.
Textile Printers & Dyers Labor Relation Institute
Triangle Publications, Inc.

Von Hoffman Press
Vulcan-Cincinnati

The Webb Corporation
Western Publishing Co., Inc.
Westvaco Corporation
Wiley & Wilson, Inc.
Henry Wurst, Inc.

Young Printing Executives Club of New York

Zabel Brothers Company, Inc.

APPENDIX C
TYPES OF CHEMICALS USED IN THE PRINTING INDUSTRY

INKS

SOLVENTS

Aromatic Compounds

Benzene
Toluene
Nylene
Ethylbenzine
Turpentine
Stoddard solvent
Varsol
Biphenyl
Orthophenylphonol
Binzoric acid
Phenol

Aliphatics

Pentane
Isooctane
Naphthenes
Maneral spirits
Naphthas
Heavy naphthas

Oxygen Containing Compounds

Methanol
Ethanol
Propanol
Isopropanol
Butanol
Isobutanol
Ethyleneglycol
Ethyleneglycol acetates
Ethyleneglycol butyrates
Acetone
Methyl Ethyl Ketone
Methyl phenyl carbinol
Acetophenne
Acetic Acid
Diethylene glycol
Urea
Glycerol

Chlorinated Compounds

Trichloroethylene
Trichloroocthane
Methylene chloride
Chlorinated paraffins
Chloroenzines

Pigment Bonding Agents

Melamine-formaldehyde
Polyacrylic acetate

Viscosity Stabilizers

Sodium nenamutaphosphate
Tetra-sodium pyrophosphate

Antifrosting Agents

Diethanolamide

Acid-Producing Agents

Acetic acid
Citric acid
Formic acid
Tartaric acid

Thickening Agents

Alginates
Cellulose ethers
Acrylamide - N-t-butylacrylamide copolymer
Dextrin
Phospheric acid estus of onyethylated wan-alcohols
Fatty acid estus of ehtylene glycol
Ethylene oxide polymers with starch
Guar germs
Gum arabic
Gum tragacanth
Polyacrylamide
Polyacrylic acids
Starches
Biosyuthetic-nanthan gums

Pigments*

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*A comprehensive list of pigments is given in *Textile Chemist and Colorist, Products/74*, Vol. 5, No. 10A (October 1973), pp. 29-95.

DISCUSSION

DR. ALBERT R. MATERAZZI (U.S. Government Printing Office, Washington, D.C.):

The statistics are in considerable need of updating; one in particular was the one on 3 percent paper spoilage.

The industry differentiates between spoilage and waste. Spoilage is that which is done in error and waste is engineered into the system--in trim waste, paper left on cores, outside wraps, running allowances, etc. And, that figure runs closer to 20 or 25 percent, unfortunately.

22 September 1975

Session I:

PRINTING PROCESSES AND CHEMICALS USED

Bohdan V. Burachinsky, Ph.D.[*]

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[*] Vice President, Corporate Research and Development, Inmont Corporation, Clifton, New Jersey

SESSION INTRODUCTION

Bohdan V. Burachinsky, D.Sc.
Session Chairman

One of the objectives of this morning's session is to set the stage for this conference by first describing the industry and defining the various printing processes and then by listing the chemicals used and/or omitted from each of the processes. Furthermore, several applicable EPA pollution control regulations and standards for emission of effluents will be discussed.

Our panel of speakers is composed of representatives of a research organization, a trade association, a Federal Government agency, and a large city department. I am sure this variety of background and viewpoints will provide for quite an interesting session.

I represent an important supplier of chemicals to the printing industry, but more importantly, I represent a technical arm of the National Association of Printing Ink Manufacturers. On behalf of that association, I would like to make a few comments. NAPIM is a technical institute which long ago recognized the crucial importance of the environmental aspects of our industry. Thus, NAPIM created a committee that concerns itself with pollution of air and water, toxicity of products in effluents, safety and industrial hygiene in our plants, recycling of wastes, and dissemination of the data and general information.

The fruits of the effort by this committee may be summed up. To date we have issued a raw materials handbook, probably the first in the industry to indicate hazards, suggestions, and handling procedures for commercial solvents. Later, plasticizers will also be described in a separate handbook. Eventually, we will also publish a booklet on pigments.

NAPIM has also conducted a study of lead- and other heavy-metal-containing pigments. This was done in a joint effort with Dry Color Manufacturers Association. We have tried to determine various hazards of and the important impact of elimination of lead-containing pigments from printing inks. We have also worked on safety standards for use of equipment and handling of potentially toxic or irritative substances in our plants.

NAPIM has worked closely with NIOSH on a simplified approach to gathering data on printing ink ingredients. NIOSH had studied and still is studying exposures to chemicals where men work. We have closely cooperated with NIOSH and devised a model-formula approach whereby proprietary information or proprietary formulation of member companies was protected. The information was offered to NIOSH, and at the same time a tremendous amount of time was saved in decoding the various formulas. So, when the industry, industry associations, and the government agency had met and found a good cooperative spirit, results were good, and objectives were accomplished.

It is clear, therefore, to me that formation and support of capable technical organizations by the various trade organizations is now very timely and quite an important step toward eliminating duplication of costs and pooling scarce human resources, especially by the more fragmented and smaller industries. There is the need for the various sister trade organizations to cooperate and collaborate closely among themselves on the safety and environmental aspects.

However, I think that government agencies and industry organizations must work very closely, openly, and professionally in order to establish the required controls and realistic standards, and to truly protect the public, the worker and the consumer without unnecessarily harming, or even eliminating any segments of our industries.

I would like to paraphrase Professor John McKetta of the University of Texas. He writes that there are still some companies and cities today that put toxic gases and liquids into our air and streams. On the other extreme are those people who wish to have distilled water in the stream and zero particulate in the atmosphere. These are impossible concentrations and could not be achieved even if there were no people on this earth. McKetta says further that the answer, obviously, is somewhere between the two extremes. We must have clean air to breathe and clean water to drink--not distilled water, not absolutely pure air, but odorless, nontoxic, clean, and healthy ones.

Actually, all of us, by driving a car, operating a press, smoking a cigarette, or swallowing a medicine, are undertaking a risk. The question may be asked, is the risk a reasonable one? Mr. Pittle of the Consumer Products Safety Commission has offered a very fine definition of reasonable risks worth, in my opinion, adapting to environmental studies. Such risk is one where the consumer or the user: 1) understands by way of adequate warning or by way of public knowledge that risk is associated with a product or a process; 2) understands the probability of occurrence of an injury; 3) understands the potential severity of such an injury; 4) has been told how to cope with the risk; 5) cannot obtain the same benefits unless risking ways at the same or less cost; 6) would not, if given a choice, pay additional cost to eliminate or reduce the danger; and finally, 7) voluntarily accepts the risk to get the benefits of the products or the process.

We here, of course, would like to communicate, to protect those who do not now, do not understand, have no choice or means, or are not here yet to protect themselves from unreasonable risks.

FEDERAL WATER POLLUTION CONTROL ACT - AN ASSOCIATION'S RESPONSE

Thomas J. Dufficy*

Abstract

Virtually all of U. S. industry has been affected and will continue to be affected by Federal, State, and local environmental regulations. This paper will review the impact of the Federal law and regulations, discuss the areas of plant inspections and trade secrets. The activities of the National Association of Photographic Manufacturers in environmental matters will also be discussed in relation to how an industry can input to the formulation of regulatory guidelines.

I am very pleased to be here this morning and share with you some of the concerns of our association and some of our accomplishments relating to the environment. I would also like to outline how we have handled plant visits and trade secrets in relation to effluent limitations guidelines. But first, let me tell you something about the National Association of Photographic Manufacturers.

NAPM is a voluntary trade association composed of companies domestic to the United States. We represent over 90 percent of the photographic industry on a dollar and volume basis.

The U. S. photographic industry is the world leader--we supply 62.5 percent of the world's photographic needs--with Japan second and Germany third. In 1973, in the amateur area alone approximately 6 billion "snapshots" were taken. You as a group do not have to be told of the tremendous photographic uses in microfilm, professional and still-motion pictures, aerial and medical X-ray, and the graphic arts.

The photographic industry has historically been interested in pollution control. In the manufacture of film or cameras or in photoprocessing, an ordinary thing like a speck of dust can be a very unwanted pollutant. Several years ago, the NAPM formed a committee to look into the environmental impact of photographic chemicals. Our initial and major thrust was in the area of water pollution control.

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*Attorney at Law, National Association of Photographic Manufactuers, Harrison, New York.

All of you are aware of the legislation that is designed to clean up our Nation's water. The Water Pollution Control Act of 1972 was enacted in an effort to get on with the job of cleaning up. The legislation prior to that amendment was geared to water quality standards for navigable waters. In pre-1972 law, if the pollutants discharged into a receiving water reduced the quality below permissable levels, legal action could be commenced against the discharger. A causal relation had to be established between the alleged polluter and the unacceptable water quality. Over a span of 20 years, very few cases reached the courts.

The 1972 act replaced all of the previous legislation, including the Water Quality Act of 1965, the Clean Water Restoration Act of 1966, and the Water Quality Improvement Act of 1970, all of which had been amendments of the Federal Water Pollution Control Act first passed in 1956.

The objective of the 1972 act is to restore and maintain the chemical, physical, and biological integrity of the Nation's waters. Several goals were established:

1. The National goal that the discharge of pollutants into the navigable waters be eliminated by 1985.
2. The National goal that, wherever attainable, an interim goal of water quality which provides for the protection and propagation of fish, shellfish, and wildlife and provides for recreation in and on the water be achieved by July 1, 1983.

I do not intent to get into any detail concerning the various levels of standards and guidelines under which permit conditions become tougher and tougher, culminating in the "zero-discharge" condition.

As you are all aware, new sources under Section 306 (b) (1) (B) will be required to apply the greatest degree of effluent reduction achievable, through application of the "best available demonstrated control technologies, processes, operating methods or other alternatives, including, where practicable, a standard permitting no discharge of pollutants."

Existing sources Section 301 (b) of the act provides:

-Not later than July 1, 1977, effluent limitations for point sources, other than publicly owned treatment works shall require the application of the best practicable control technology currently available.

-Not later than July 1, 1983, effluent limitations for categories and classes of point sources shall require application of the best available technology economically achievable.

In light of the foregoing regulations, what did the photographic industry do? We knew that the EPA, the States, and the municipalities would eventually be looking at our industry. Quite a large amount of information was around, but not in any cogent form. We at NAPM felt we were in a good position to commission a study, and one was started over 3 years ago. Hydroscience, Inc., a very respected firm in the wastewater area, conducted the study of some 45 chemicals commonly used in the photoprocessing industry. It is now complete and published in two volumes.

The effects of the 45 chemicals on conventional biological wastewater treatment systems and on representative aquatic organisms were studied through a multiphase program. Also included in the study were: 1) determination of the responses of the chemicals to analyses common to wastewater management, 2) investigation of the impact of a combined photoprocessing effluent, and 3) the development of a simplified dilution model to predict approximate downstream concentration of various constituents discharged to receiving water.

The study yielded four major conclusions. The first is that on the basis of information developed during the study, it was determined that photoprocessing wastes do not present a hazard to biological systems encountered in conventional wastewater treatment schemes or to aquatic organisms indigenous to natural receiving water systems. The assumption inherent in the above statement is that a photoprocessing waste is not directly discharged to a natural receiving water without adequate treatment before discharge.

The results indicate that photoprocessing wastes are amenable to biological treatment, with a removal efficiency approximately equivalent to that encountered with domestic wastewaters. The concentrations expected to occur in municipal or regional sewerage systems and in a receiving water upon treatment will not adversely affect biological systems.

The second conclusion is that the 45 photoprocessing chemicals investigated in this study have no significant impact on the activity or efficiency of the biomass of a conventional biological wastewater treatment system, at the concentrations realistically attainable in municipal or regional sewerage systems. The chemical concentration expected to occur in the discharge from a photoprocessing laboratory may be estimated by applying a one-hundredfold dilution to the working solution concentrations.

Bioassay experiments were conducted to determine the impact of the photoprocessing chemicals on aquatic organisms representing different levels in the food chain. The experimental results led to the third conclusion that, at the concentrations estimated to occur in the receiving water at the point of discharge from a municipal biological treatment plant, none of the photoprocessing chemicals examined would adversely affect the types of organisms represented by the test species.

Fourth, there is no typical photoprocessing waste. Each photoprocessor represents a unique combination of processes and modes of operation. The list of chemicals chosen for study was certainly not all-inclusive, but it is judged that the selected chemicals are representative of many commercial processes and that the results of the study could be applied to other chemicals of a similar nature. The Kodak E-4 color reversal process waste, specifically used to evaluate the impact of a composite photoprocessing effluent, for instance, is not typical, but is considered to represent a broad cross section of chemicals used in photoprocessing.

After the Hydroscience study was completed, we ran several seminars in New York, Chicago, and Los Angeles to disseminate the information and also to provide regulatory people in the industry with some basic information on what the photoprocessing effluent looks like and how to treat it.

Just as our study was winding up, two developments of interest were taking place. First, EPA was getting ready to award a contract for the development of effluent limitations guidelines and standards of performance in the miscellaneous chemical area. Miscellaneous chemicals were divided into eight industries, the photographic processing industry being one of the eight and being composed of the following SIC codes: 7221--photographic studios; 7333--commercial photography, arts and graphic; 7395--photofinishing laboratories; 7819--developing and printing of commercial motion picture film. The contract was awarded to Roy F. Weston; a draft development document has been circulated and the NAPM has submitted comments.

The second development of interest was the awarding of a contract for effluent limitation guidelines in the machinery and mechanical products manufacturing area. Photographic manufacturing was included in this basket study, which included some 175 separate industry categories. The list included steel foundries, plumbing fixtures, ammunition, electric lamps, and ended, perhaps significantly, with SIC code 3995--burial caskets.

This contract was awarded to Hamilton Standard, which has submitted its four-volume draft development document for comment. One thing you will find is that EPA is under some unreasonable time pressures and that it passes the unreasonableness on to the industry. Comments were to be made by August 29th--we did not make the deadline. We are meeting in 2 days to finalize our comments.

This brings me to a very important part of the whole procedure--the comments on EPA's proposed regulations. I think all parties will agree--and I include the various regulatory bodies, industry, and other interested persons--that it is much better for all concerned that issues be settled at the administrative level. Most trade associations and companies try to make their best case with the agency. We all know it is much harder to change proposed rules than to get good rules proposed in the first place. We at NAPM have been spending our time in developing data upon which good rules can be established. If a case does get into the court system, the most that can be expected initially is a remand. The courts for the most part are unwilling and unable to write new regulations.

Courts that review the regulations of government agencies do not take testimony; the record is all the evidence that they can use to decide the case. It is of course imperative that the record be complete on both sides of the issue. To that end, we have urged our members to cooperate fully with EPA. We have had some minor problems involving nondisclosure arguments, but in general things seemed to have worked out.

We have urged our member companies to develop data and information that can be used to challenge a point. We want specific items, not generalizations. We always ask for split samples; we have challenged analytical results, flow rates, and descriptions of processes.

We assume, and I believe correctly, that EPA and its contractors are professionals who are seeking to do the best job humanly possible. We are trying to help them.

There are, of course, many considerations that a company must make prior to the disclosure of certain facts and figures. In addition, there seems to be a continuous movement toward full disclosure. Perhaps this is due to the influence of the Federal courts, which have a long history of requiring that all of a litigant's case be included on record prior to a trial, through the use of discovery proceedings.

In the case of effluent guidelines, you can look at the so-called Supplement B, which contains the working papers and data that formed the basis of the contractor's draft development document. We shall soon see if the regulations reflect any industry input.

There are such things as proprietary formulas, production data, new products, manufacturing processes, and information of that nature that ordinarily will come into the hands of EPA or its agents in the course of running various EPA programs. And all of us are aware that industrial competitors, both foreign and domestic, would very much like to have any information they can get.

EPA proposed regulations for the treatment of trade secrets and confidential data in May 1975; these were scheduled to go into effect sometime in July. The EPA regulations include a requirement that it is the responsibility of a business which makes a confidentiality claim to substantiate that claim. EPA in its part must allow a reasonable time for the business to do so, and it should honor a demonstration of confidentiality in releasing the information gained. Furthermore, judicial intervention should be a consideration in an injunctive relief type of situation.

It has been our experience that the EPA program sounds good but has many areas of possible breakdown and that it overlooks some areas. One thing that might be done is to establish a requirement that any contractors performing work under an EPA contract execute a secrecy agreement. This would restrict the disclosure of any technical information not in the possession of the contractor prior to the date of disclosure to all but EPA. The agreement would have certain provisos to lift the restriction if the data is available from other sources, etc.

In addition to providing input to the creation of government regulations, NAPM has been involved in the development of national standards. Any competent chemist can tell you that analytical methods can yield erroneous results in the presence of certain "contaminants"; I believe these results are called "interferences." However, the standard analytical methods employed by chemists have most of the probable interferences eliminated, or else ways have been found to obviate their effects. The term "most probable" would not include photographic chemicals because they are not significant in most industrial or domestic wastes.

NAPM is also the secretariat of several American National Standards Institute (ANSI) committees dealing with photographic standards. A committee under ANSI-PH4-5 examined the standard methods for various parameters in the light of the interferences that could be expected from photographic chemicals. The committee also examined analytical methods for classes of chemicals such as phenols to establish whether the specific compounds used in photography would respond to the standard methods; some do not.

ANSI Committee PH4-5 developed a standard that furnishes or refers to acceptable analytical methods for analyzing photographic processing wastes. Included in the standard is an appendix with detailed analytical methods for the following situations: 1) where no method exists in the standard reference sources; 2) where it is necessary to provide for pretreatment, etc., to eliminate interferences likely to be present in photographic wastes; 3) where it is necessary to provide methods that are not affected by interfering photographic chemicals, as are the published standard methods. The standard also includes some other methods, such as "ferrocyanide in photographic waste effluents and the determination of the chlorine requirement of photographic processing effluents."

One of our ANSI committees is working on a guide to effluent management for photographic processing facilities. It is not yet close to publication; we have decided to wait and see what the effluent guidelines for miscellaneous chemicals say, and we will then tailor the guide accordingly.

The format of the guide should be helpful. We are going to give some brief information on the Water Pollution Control Act of 1972--how it will effect the photoprocessor, how the States and localities come into the picture, and some of the key dates. The guide will provide checkoff lists for effluent characterization, where the discharge goes, and some basic ideas on how to start an effluent management system.

The guide will be intended as a preliminary approach to defining a particular effluent problem. Where answers are general in nature, they will be supplied; where the information is specific, appropriate space will be provided for calculations and insertions of data. A bibliography and directory will be included for further information.

This wraps up my presentation. I hope that hearing about the NAPM's response on behalf of its members to the Water Pollution Control Act of 1972 will be of help to you in meeting similar challenges.

DISCUSSION

MR. SALTZMAN (Bureau of Solid Waste Management, New Jersey Department of Environmental Protection, Trenton, New Jersey): Consideration, as I understand, is being given to taking the wastes and treating them prior to taking them to municipal disposal facilities. Is consideration being given to taking these wastes and disposing them in, say, class 1 chemical dump facilities or disposal facilities?

MR. DUFFICY: Consideration is being given to that. And that, of course, is going to depend on the locale and what its situation is from an economical standpoint.

I did not mention it in my talk, but we have recently commissioned a study looking into leaching characteristics. Part of the study is going to be a lysimeter test, just to see what happens to silver and ferricyanide, what happens to an inland fill, things of that nature. This is something that is being considered.

Most of the photoprocessors do have all kinds of pretreatment going now, silver recovery being one, bleach regeneration being another. And they are continually trying to make their particular operation as economical as possible. They're doing it in plants right now, in most places.

CHAIRMAN BURACHINSKY: Are there any other questions?

MR. WILLIAM S. BEGGS (New Jersey Department of Environmental Protection, Trenton, New Jersey): I wanted to ask you about the 45 chemicals that you have. Do you have a brochure on that?

MR. DUFFICY: Yes.

MR. BEGGS: I would like to get a copy of it.

MR. DUFFICY: This is the brochure. I would like to hold onto it for just a little while. This comes in two volumes--Volume 1 and Volume 2. We have provided it to regulatory people--EPA; the State; the New Jersey Department; the various governmental agencies; Departments of the Army, Navy, Air Force, etc.--free. We thought it would be worth our while to get it to them. We charged anyone else $25. If anyone would like any of this information, get in touch with us. Are there any other questions?

CHAIRMAN BURACHINSKY: I would like to modify my comment that every trade organization, besides having a good technical arm, should not forget to have the services of a competent and experienced attorney.

HYDROCARBON EMISSION REGULATIONS

James A. McCarthy*

Abstract

Future hydrocarbon emission regulations will have impact on the plans and profits of the printing and related industries. This paper presents background information on hydrocarbons, their effects, and current thinking about their control. The author presents his views on future trends in hydrocarbon regulations.

It is a pleasure to meet with you today to discuss hydrocarbon emission regulations. This is a subject in which I believe many of you will be interested because the levels and extent of future hydrocarbon regulations could have an impact on both the plans and profits of the printing and related industries. During my talk, I will review some background concerning hydrocarbon emissions, their effects, and past regulatory efforts. Then I will discuss current thinking about hydrocarbon emission control. Finally, I will describe what I see in the future for hydrocarbon control.

First, I think it would be valuable to describe briefly our organization and my part in the overall picture. I am in the Control Technology Office of the Emission Standards and Engineering Division of EPA. EPA's offices at Research Triangle Park, North Carolina, have a prime responsibility for EPA activities in controlling air pollution from stationary sources. We are partially responsible for approving State air pollution regulations and for technically assisting State agencies. We are also responsible for developing air pollution standards for new sources, an area that is assuming greater significance in terms of the nationwide goal to clear the air.

Let me begin by answering a few commonly asked questions. One of the most frequent is: why control hydrocarbons? The answer is, very simply, to reduce oxidant concentrations in the air we breathe. Oxidants, including ozone, are the main irritants in photochemical smog. Oxidants are formed in the presence of sunlight by the reaction of organic compounds from fuel combustion, solvent evaporation, and industrial processes with nitrogen oxides from fuel combustion processes. The reaction products--oxidants--are not only dangerous to man and animals, but also adversely affect vegetation and materials such as rubber, cotton, nylon, and polyesters.

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*Chemical Engineer, Environmental Protection Agency, Durham, North Carolina.

Another question is: what are hydrocarbons? Strictly speaking, a hydrocarbon is a compound containing only carbon and hydrogen atoms. In actuality, however, we are concerned with any gaseous organic compound emitted into the atmosphere in sufficient quantity to pose a potential oxidant problem. Many people refer to this group of compounds as hydrocarbons for simplicity.

Lastly, how does printing contribute to the overall problem? Of the more than 25 million tons of hydrocarbons estimated to be emitted nationwide each year, stationary sources of all types contribute about one half. Of that quantity, printing represents a small percentage. The printing industry is, however, localized and, in certain metropolitan areas, is a significant source. A larger emission source, with which some of you may be involved, is paper coating.

Hydrocarbon emissions are typically reduced in two ways. First, control devices can be added to recover the hydrocarbons from the exhaust stream or to convert them, by incineration for example, to a less noxious state; or second, processes or materials can be altered in such a way as to reduce or limit the use of hydrocarbons. Each way has advantages and disadvantages. Add-on devices usually represent nonproductive capital expenditures, but can be implemented fairly rapidly. Process or material changes, while more efficient and less costly, can affect final product characteristics. The decision to use any specific system must be made in light of all available technical and economic information.

Air pollution control agencies and the Congress have developed mechanisms by which controls can be instituted and emissions consequently reduced. The Environmental Protection Agency's air pollution effort is based on the Clean Air Act of 1963. The Clean Air Amendments of 1970 were a major revision to the Clean Air Act, and there were minor changes in 1974.

Under the Clean Air Act, the system works like this. EPA establishes ambient air quality standards for proven adverse air pollutants. A national ambient air quality standard is the maximum level of a pollutant which will be permitted in the ambient air, i.e., the air we breathe. These standards apply to specifically designated pollutants known as "criteria pollutants."

In April 1971, the Environmental Protection Agency promulgated national ambient air quality standards for six pollutants, including photochemical oxidants and hydrocarbons. States then prepared implementation plans describing the controls required within their jurisdictions. Variations are expected owing to the difference in sources, emissions, existing air quality, and meteorology between States. Required time frames are also outlined, with certain deadlines being required by the act. EPA then passes on the adequacy of State plans. We cannot make State plans less stringent, but we must tighten plans if necessary to insure that ambient air concentration goals are met.

The act also requires that EPA develop emission standards for new sources, but it gives EPA the discretion to select and move as it sees fit. The key was that Congress believed that new sources should use the best available control technology, taking costs into account, and that the latest technology should be installed when new plants are built, even when it is not necessary to meet the ambient air quality criteria. This was and is believed to be the most effective and least expensive way to prevent major air pollution problems from recurring in the future.

New source performance standards have been set for 13 industries and proposed for 10 others. Studies are underway by EPA on another 30. Only one new source performance standard involving hydrocarbons has been promulgated or proposed to date, that for large petroleum liquid storage vessels. However, in the current group of 30 industries being studied are several involving hydrocarbons. I will discuss these a little later.

Two points should be emphasized with regard to new source performance standards. First, best available control is meant to emphasize new technology, not rely on the old. Second, a new source, as defined, not only refers to newly constructed facilities, but also includes existing facilities when they are modified if such modification results in an increase in the emission of an air pollutant.

It is also important to stress that States have a great deal of authority over which EPA has little direct control. We serve in many instances as a source of technical information for the States. We can, and often do, make engineering recommendations, but the burden is on the States to control existing sources.

Hydrocarbon control strategies are in a state of evolution. In past years photochemical smog was believed to be primarily an urban problem, and control was oriented toward that end. For example, Los Angeles County limited emissions of the more photochemically reactive materials in order to attack its local oxidant problem. The slower reacting materials are called "exempt" solvents. Furthermore, automobiles were considered to be the principal emitters of hydrocarbons so that controls relied heavily on the Federal Motor Vehicle Control Program. However, as more and more data are being gathered, it is becoming apparent that strategies emphasizing control of only the most reactive local emissions, or those concerned mainly with automotive emissions control are not entirely satisfactory. Let me give you some specifics.

First, it has been found that emissions from stationary sources cannot be neglected. They are larger than was initially realized and represent an ever increasing fraction of the total pollution problem as more and more automobiles with hydrocarbon controls replace older automobiles with less control.

Second, high concentrations of oxidants have been found in basically rural areas and at considerable distances downwind of urban areas. This seems to indicate that oxidants are moved or formed over wide areas of the country. In time, almost any organic will react. Thus "exempt" solvents contribute to oxidant problems in distant locations.

Third, world situations are changing. Energy supplies and costs are crucial factors that must be considered.

It is becoming clear that: 1) oxidants are a stationary source problem, in addition to being a mobile source problem; 2) oxidants are a national, not just a local problem; and 3) EPA must focus much more of its attention toward resolving these issues along with considering the costs and availability of fuel.

EPA is mounting a major new effort aimed at developing and promulgating performance standards for significant emitters of hydrocarbons. Standards have been promulgated for petroleum storage and gasoline marketing. Also underway are studies of the drycleaning and degreasing industries. Most importantly for you, we are also in the process of initiating a major study of the industrial surface-coatings industry, including paper and paperboard coating. Engineering studies will narrow the scope to a manageable number of significant emitters, and then detailed engineering, economic, and environmental impact studies will be performed in order for new source performance standards to be developed. By late 1976 or in 1977 these new source performance standards may be proposed.

EPA will supply our regional offices and State and local officials with a continuing dialogue in an effort to keep them abreast of new, demonstrated technology and to make recommendations for their future actions. Both printing and paper and paperboard coating will come under closer scrutiny by State officials.

I also strongly suspect that, in the near future, some States will begin to move toward emphasizing new coatings technology and away from add-on controls and the use of "exempt" solvents. I expect "exempt" solvents to be allowed as an interim control option, but only if no other reasonable option is available. It seems clear that in the long run "exempt" solvents as the sole control method will be phased down significantly.

In summary, hydrocarbon control regulations over the past few years have been turbulent and confusing. I wish I could tell you that this situation is resolved. I cannot. The future will also be turbulent, but I firmly believe that we are in the process of developing more rational approaches to solving the many problems, and you can soon begin to plan your future thinking in terms of pollution control with more confidence. EPA will work with you, through our regional offices and our engineering and enforcement activities. We are always available to help you solve your problems in as equitable a manner as possible.

We collectively face a very great challenge, but it is a challenge that we can meet if we work together.

DISCUSSION

MR. ED J. HEISER (Dow Chemical, U.S.A., Midland, Michigan): You mentioned a study to include paper and paperboard coatings. Are you talking about hydrocarbon emissions from these test applications?

MR. McCARTHY: Yes.

MR. HEISER: Because coatings cover this application, aqueous system, too?

You are not considering that?

MR. McCARTHY: We are considering aqueous systems. In some aqueous systems you have some solvents or a monomer emission of an aqueous polymeric application. And that is a hydrocarbon emission. Paper and paperboard coating is not my specific area, but I understand a lot of it involves adhesives. A lot of hydrocarbon emissions are from the application of adhesives. But I understand that even the water-base systems have a monomer emission problem.

DR. WILLIAM D. SCHAEFFER (Graphic Arts Technical Foundation, Pittsburgh, Pennsylvania): Is it in order for you to say anything about EPA's prospective on Congressional actions within the year or next year in the extension of the action?

MR. McCARTHY: I really have not even seen the latest markup of the act. I do not think it is going to have a significant effect on us. I think it is going to make EPA more flexible in meeting deadlines. We have more flexibility to work and make the deadlines more reasonable. That is my understanding of what is happening.

MR. BILL MAGIE (Magie Brothers Oil Company, Franklin Park, Illinois): How have you determined that some of the exempt solvents eventually do become photochemically reactive?

MR. McCARTHY: Well, the way that they rank solvents as exempt in the first place is by testing them in test chambers--smog chambers--where they simulate the action of sunlight, NO_x, and hydrocarbons. Some compounds just react immediately. I think the criteria was something like less than 6 hours was considered to be a reactive solvent, meaning that in a 1-day type situation it would turn into oxidants. If you keep compounds--really, anything but methane and probably the fluorinated compounds and a few others--in there long enough, they react. You can measure that they do. Over a week or 2 weeks, they all react. So it is experimental empirical evidence that says that all these compounds react to form oxidents.

MR. WILLIAM S. BEGGS (New Jersey Department of Environmental Protection, Trenton, New Jersey): Most chemical reactions are chain reactions. You are speaking about the immediate reaction with sunlight to produce these smog-producing chemicals. It seems to me that there is also another aspect of it; that is, the destruction of the product. In other words, in a sense it is an intermediate--

MR. McCARTHY: I'm sorry, I'm not following you.

MR. BEGGS: We know that most chemical reactions are chain reactions.

MR. McCARTHY: Right.

MR. BEGGS: There is the effect of sunlight, and then reaction with NO_x to produce an oxidant, you see. Now then because of the varied activity of these things, they degrade further, presumably to carbon dioxide, so that you have the building up of these oxidants and their destruction at the same time. The concentration of any one oxidant would therefore be determined by the rate constants of its formation and its destruction. Have you made any studies along these lines?

MR. McCARTHY: There are a lot of problems involved when simulating happens in the atmosphere. There has been criticism with what they do in smog chambers as being much too intense. For reasons of measurement techniques, they usually use concentrations in a small chamber that are not typical of what is found in an urban atmosphere. I think they have done some recently with some sophisticated instruments where they do use very low concentrations. They do know what the end products are. Carbon dioxide is formed; ozone is formed. Ozone will react with almost anything.

THE ORGANIC EMISSION PROGRAM OF CHICAGO

George T. Czerniak,* William Thorp,
and Philip Byron

Abstract

The information presented in this paper is directed to those interested in the program undertaken by the City of Chicago to implement its Organic Emission Ordinance. After the adoption of the ordinance in May of 1974, the Department of Environmental Control developed a program of data collection. The purpose of the program was to determine whether or not a company was in compliance and to update the Emission Inventory. Discussed in the paper are the procedures of data collection, data analysis, and control programs for noncompliant sources.

INTRODUCTION

BACKGROUND

The term air pollutant, when considered strictly, includes any substance not normally found in the air in significant concentrations. However, the connotation of the term has come to include only those substances which have detrimental effects on life. Organic gases are considered to be air pollutants under this definition.

Organic gas emissions occur primarily as the result of the incomplete oxidation and cracking of fuels during combustion. There is also a significant contribution by the evaporative losses of liquid organic materials.

The major interest in organic gas emissions stems from their ability to participate in atmospheric photo-oxidation reactions. Organic gases, in the presence of oxides of nitrogen, react under radiation from the sun to form various substituted organics. Many of these intermediates are associated with the irritating effects of photochemical smog.

As far back as the 1940's, Los Angeles County enacted the first regulations designed to deal with the problem of organic emissions. These

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*Environmental Control Engineer, City of Chicago Department of Environmental Control, Chicago, Illinois.

regulations evolved into their present "Rule 66." This rule took into account the varying reactivities of different classes of organic compounds and limited the emissions of formulations containing over certain percentages of these classes.

On May 29, 1974, the Chicago City Council adopted an amendment to Chapter 17 Article IIC of the Environmental Control Ordinance of the Municipal Code of Chicago entitled "Control of Emissions of Organic Substances." This amendment regulates the storage and handling of organic material as well as emissions from stationary sources. Although similar in intent to the Los Angeles County and State of Illinois regulations, the specific language of the Chicago ordinance required some different interpretations. These will be discussed later.

GOALS OF ORGANIC EMISSIONS SURVEY

The adoption of the new ordinance necessitated that the Chicago Department of Environmental Control institute a plan to bring all companies in the city into compliance. This plan was called the Organic Emissions Survey. Other objectives of this survey were:

1. To update the previous annual emission inventory figures to more accurately reflect solvent emissions by company and arrive at an organic emission figure for the city.
2. To organize and maintain the collected data to be useful in any future studies of atmospheric photo-oxidation reactions and their related effects.

SCOPE OF ORGANIC EMISSIONS PROGRAM

Organic emission survey forms were first sent to companies emitting at least 2,000 gal/yr according to the 1973 and 1974 emission inventories. The 2,000 gal/yr cutoff point was chosen for two reasons: 1) When averaged over and 8-hr work day and 250 d/yr, this figure would not produce in excess of 8 lb/hr solvent emissions (even if there is only one emission source in the plant); 2) The contributions by many low-usage companies to the total emissions are minimal and the man-hours necessary to gather and analyze the additional data would not be justified by the amount of information gained.

Assuming that all large emitters were accounted for on either the 1973 or 1974 emission inventory, it can be said that this survey will provide an accurate picture of solvent emissions from industrial stationary sources in Chicago.

ATTITUDE OF PROGRAM

Once the goals of the Organic Emissions Program were established, it was necessary to develop the proper administrative attitude which would enable us to swiftly realize those goals. It was felt that a cooperative attitude, would be more likely to give the results that we required in the shortest period of time. In keeping with this, the department functioned as an advisor to the companies in the following capacities: assisting in the completion of the appropriate forms; advising the companies on the alternative means of achieving compliance; guiding companies through the steps necessary to allow time to achieve compliance.

INTERPRETATION OF ORDINANCE

The first major task necessary to the development of the Organic Emissions Survey Program was to gain an understanding of the adopted ordinance. This was made difficult in some portions because the intents were not clear or seemed to be at odds with the specific language of the ordinance.

For these particular portions, an interpretation had to be made which would be compatible with the overall intent of the amendment and yet follow the specific language closely enough as to be enforceable. These portions are listed in exhibit 1.* The first column of exhibit 1 is the section of the ordinance as it was adopted. The second column gives a clarification of the stated section. The third column gives examples and applications if necessary.

METHODS OF SELECTING COMPANIES TO BE SURVEYED

The companies that were surveyed were selected based on the solvent emissions from the 1973 emission inventory. A "Hydrocarbon Data Form" (copy included as exhibit 3) and an accompanying cover letter (copy included as exhibit 2) were mailed to the selected companies. In order to distribute the work load associated with processing the data forms, the forms were first mailed to the major solvent emitters. This enabled rapid collection of data relating to the majority of solvent emitted.

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*All exhibits are located in the appendix.

During August 1974, 12 companies were required to complete the Hydrocarbon Data Form. In addition to the collection of emission data, the purpose of these forms was to obtain feedback concerning the form itself. As a result of this feedback, the "Hydrocarbon Data Form" was modified slightly.

During October 1974, companies whose solvent emissions were 6,000 gal/yr or greater were required to complete the Hydrocarbon Data Form. Therefore, an additional 107 companies were required to complete the form. Included in this category were 31 companies engaged in some form of printing.

During March 1975, a modified version of the Hydrocarbon Data Form was sent to 134 firms whose solvent emissions were greater than or equal to 2,000 gal/yr and less than 6,000 gal/yr.

During the summer of 1975, the 1974 annual emission inventory was completed. The 1974 emission inventory listed 70 additional companies whose solvent emissions were 2,000 gal/yr or greater and who had not been included in that category in the 1973 emission inventory. These companies were mailed forms in August of 1975. In addition to the above mentioned requests for data, other requests were made at various times. These added companies were not listed on the current emission inventory and were brought to our attention by the Annual Survey Section.

FORMS USED TO COLLECT DATA

The Hydrocarbon Data Form is a questionnaire designed to determine the compliance of an industrial facility with Chapter 17, Article II-C. The form dealt with five sections of Article II-C that past experience indicated were applicable to industrial facilities in Chicago. The general topics covered in each of the five sections are:

Section I	Storage of organics;
Section II	Loading of organics into a railroad tank car, tank truck, or trailer;
Section III	The use of an oil/water separator;
Section IV	The use of liquid organic material in a process;
Section V	The use of a vapor blowdown or safety relief valve set.

After obtaining feedback concerning the form from 12 companies that were required to complete the form during August 1975, the form was modified slightly. During October 1974, additional companies were required to complete the form.

Later, after analyzing the data submitted on the forms and the companies' reactions, the Hydrocarbon Data Form was modified and renamed the "Organic Emission Data Form." Basically, the modifications consisted of: 1) deleting Section II, III, and V, since there was a negligible number of companies involved with processes covered in these sections, 2) changing the format of the section dealing with the use of liquid organic material in a process, in order to simplify the completion of the section; and 3) adding a number of questions concerning plant operation, and status before other environmental control agencies. The purpose of the modifications was to make the form easier to complete and to obtain additional information. As a result, the Organic Emission Data Form consists of three sections dealing with the following general topics:

Section I	Storage of organics;
Section II	Use of liquid organic material in a process;
Section III	Several "yes" or "no" questions concerning plant operation, and status before other pollution control agencies.

A copy of the Organic Emission Data Form is included as exhibit 3.

FOLLOWUP ON ORIGINAL MAILING

When a company was required to complete the data form, it was advised in the cover letter (see exhibit 2) that it was allowed 30 days to complete and return the form. However, if a company requested an extension of the 30-day deadline, it was normally granted; this was necessitated when a company had to gather data (in-plant and supplier). In general, companies requested the extension by a written communication. Extensions were granted for approximately 30 days, to give the company ample time but not to let the matter slip out of mind. The companies usually acted in good faith to expedite the completion of the form. The procedure for additional extensions was the same as for the first.

Approximately 40 days after the data requests were mailed, the file was reviewed to determine which companies had not replied or requested an extension, and a followup letter (exhibit 4) was sent to these companies. This letter was a courteous reminder that the form was due, and served to advise the company that a time extension and/or assistance was available.

If a company did not respond in some manner to the first followup letter, a second followup letter was sent by certified mail. A copy of the second followup letter is included as exhibit 5. This letter advised that if the forms were not submitted within 15 days, enforcement action would be taken. In four cases, the companies did not show a good faith effort to complete the form; these companies received a citation. We are awaiting the results of the court hearing regarding these citations.

DATA ANALYSIS:
ORGANIC EMISSION COMPLIANCE

The analysis of Section II of the Organic Emission Data form was facilitated by the use of two computer programs. Those programs were written for use on the Wang 700A computer-calculator in conjunction with the IBM 701 output writer. These programs enabled a rapid determination of compliance and a breakdown of data into usable categories.

The "compliance check program" determined the following items:

1. Whether or not the coating as furnished from the supplier was photochemically reactive;
2. Whether or not a material added to the coating at the plant was photochemically reactive;
3. Whether or not the mixture of the coating and the materials added at the plant was photochemically reactive;
4. The average and maximum pounds per hour of solvent emitted due to the use of the mixture; and
5. Whether or not the mixture qualified to be exempted from the ordinance under the high-solids or water-base classifications.

Knowing which items in a mixture were photochemically reactive was helpful when discussing a possible violation with a company. If a company considered reformulation, it was advised which components of the mixture needed to be reformulated. The average and maximum pounds per hour figure was useful in determining the emissions from sources using the specific solvent.

Exhibit 6 is a copy of the format sheet used with the compliance check program. The data listed in vertical columns on the left side of the sheet are entered into the computer. This information is furnished by the company on the Organic Emission Data Form. The data listed in the horizontal rows on the right hand side of the sheet are the output from the computer, as explained above.

Exhibit 7 is a flow diagram illustrating the general logic of the compliance check program but not the detailed calculations involved in the decisionmaking. In order to clarify the definition of a photochemically reactive material, it is necessary to present the detailed calculations involved in the determination of whether or not a material is photochemically reactive. The calculation must be clarified because the definition of a photochemically reactive material specifies certain percentages by volume of designated chemical compounds. The percentage is based on the total organics, including liquid and solids, in the compound. However, the percentage availabe from a company is based on the liquid organics in the compound. Therefore, it is necessary to perform a calculation which converts the percentages given on page 9, rows 6c, 6d, and 6e of the Organic Emissions Data Form to the basis of total organics in order to evaluate whether or not a material is defined as photochemically reactive.

Following is the calculation method used to change the basis of the volume percentage of Class 1 material from total liquid organic to total organic:

Volume % of total organics = (volume % organic solvent) + (volume % solids/100) x (volume % solids organic).

Volume % of Class 1 material in the formulation = (volume % of Class 1 compounds) x (volume % organic solvent/100).

Volume % of Class 1 material based on total organics = (volume % of class 1 material in the formulation)/(volume % of total organics).

The volume percentage based on total organics of the two other classes of materials is determined in the same manner as used for Class 1 material.

DATA ANALYSIS: SUMMARY FORMS

The "Summary Program" determines the following items (all figures are in gal/yr; the bracketed phrase refers to the label given to the figure on the format sheet):

1. The total amount of formulations used (Formulation Used);
2. Total solvent contained in 1 (Potential Solvent);
3. Total solvent from 2 which is captured by a control device (Solvent Controlled);
4. Solvent emitted to the atmosphere (Solvent Emitted);
5. Total solvent emitted that is defined as photochemically reactive (PCR Solv. By Def.);
6. The total of the various classes of solvent used to define a photochemically reactive solvent contained in coatings that are defined as photochemically reactive (1,2,3 in PCR Material);
7. The total of the various classes of solvent used to define nonphotochemically reactive (1,2,3 in NPCR Material);
8. The total of each of the three classes of materials used in the definition of a photochemically reactive material--(Class 1), (Class 2), (Class 3);
9. The total of each of the three classes of materials used in the definition of a photochemically reactive material which is contained in material defined as photochemically reactive or nonphotochemically reactive; for example, Class 1 material contained in photochemically reactive material and nonphotochemically reactive material is referred to as PCR 1 and NPCR 1, respectively, on the format sheet: (PCR 1), (NPCR 1), (PCR 2), (NPCR 2), (PCR 3), (NPCR 3).
10. Total photochemically reactive solvent associated with a particular coating (B);
11. Total of each of the three classes of materials used in the definition of photochemically reactive material contained in 10: (Gal/Yr Class 1), (Gal/Yr Class 2), (Gal/Yr Class 3).
12. Total of the three classes of materials given in 11 (C).

Exhibit 8 is a copy of the format sheet used with the Summary Program. For the data listed in the vertical columns labeled 1,2,3, etc., items 1 through 20 are furnished by the company and entered into the computer. The remainder of the information on the sheet is the output from the computer, as explained above. Each vertical column refers to a single coating. The information listed in the two rows at the bottom of the sheet are totals for all of the coatings used by a company.

Exhibit 9 is a flow diagram illustrating the general logic of the Summary Program.

In order to better understand the format sheet used with the Summary Program, it is necessary to know the distinction between a) material that is photochemically reactive by definition and b) material that falls into one of the three classes of chemical compounds which are used in the definition of a photochemically reactive material. The definition of photochemically reactive material states that when an organic material consists of more than a specified percentage (by volume) of any of the three listed classes of chemical compounds, or more than 20 percent (by volume), or an aggregate of the three listed classes of chemical compounds, it is defined as photochemically reactive.

The entire formulation is defined as photochemically reactive when it meets the requirements of the definition. This is the case even though there are some exempt compounds in the formulation.

A compound included in one of the three classes of chemical compounds used in the definition of a photochemically reactive material may or may not cause the formulation of which it is part to be defined as photochemically reactive. Since these three classes of compounds have been determined to be highly photochemically reactive, the ordinance has been designed so as to control the use of formulations that contain a significant amount of these three classes of compounds. However, a formulation may contain less than the specified amounts of the three classes of chemical compounds and therefore not be defined as photochemically reactive. When a formulation is not defined as photochemically reactive, the emissions of it to the atmosphere are not regulated by the ordinance, unless there happens to be an odor nuisance.

The purpose of making this distinction is to show that even though a formulation may not be defined as photochemically reactive, it may contain a significant amount of material that in actuality is very photochemically reactive. Significant quantities of the three classes of the chemical compounds used in the definition of photochemically reactive material are emitted from processes which are in compliance with the ordinance. This compliance is achieved by either the formulation being nonphotochemically reactive by definition, or the emissions of the formulation being less than 8 lb/hr from each emission source, or the use of a control device. The point to be considered here is that the emissions of reactive material in compliance with the ordinance will most likely not be reduced, because in general the reactive material is less expensive and more readily available than nonreactive material. Also to be considered is the fact that when a noncomplaint formulation is brought into compliance through reformulation, the emission of the three classes of chemical compounds used in the definition of photochemically reactive material will be reduced, but the reduction will not necessarily be 100 percent.

DATA ANALYSIS:
COMPLIANCE OF OTHER SECTIONS OF THE FORM

Analysis of Sections I and III of the Organic Emission Data Form was made by inspection. The company's specific situation was reviewed in light of the applicable regulations. This approach was used because each situation varied and it was therefore not practicable to use a computer method.

CORRECTIVE PROGRAMS

When it was determined that a company could possibly be in violation of the Organic Emission Ordinance, the company was requested to attend an informal meeting in the department's office to discuss the matter. At the meeting, the information submitted on the data form was verified and the process using the photochemically reactive material was discussed. It was necessary to verify the data because a company may have changed its material since the form had been completed or the company may not have interpreted the data form correctly.

The process using the photochemically reactive material was discussed in order to determine the nature of the process, the type of equipment used, and the rate of material usage. The process itself may affect total emissions due to solvent retention.

Important considerations regarding the equipment are the number of pieces of equipment and associated vents to the atmosphere. In some cases, a company used a photochemically reactive material in a number of machines, each with its own vent to the atmosphere so as to allow each machine to be defined as a source. In these cases, the companies may have been emitting a substantial amount of photochemically reactive material; however, they were not in violation since no one source exceeded the ordinance limitation of 8 lb/hr. Another important consideration is the sequence in which the equipment is used. Application areas, conveyors, and drying or baking devices may be used in various sequence. The location of the emission will be affected by the "flash off" rate of the material and the flash off forced by a piece of equipment, as well as by the equipment sequence. For example, during a conveyor spray coating operation, solvent will "flash off" in the spray booth, on the conveyor to the drying oven, and in the oven. If the coating has a high flash off rate, as lacquer does, a majority of the solvent in the lacquer will flash off immediately in the booth. However, if the coating has a low "flash off" rate, such as an enamel, a substantial portion of the solvent will remain in the coating until it is forced to flash off in the drying oven.

Material usage was discussed to determine the rate of usage associated with each piece of equipment. In most cases, when a company used several pieces of the same type of equipment, the usage rate of various pieces varied. For example, one piece may be for touch-up or special work.

After the discussion relating to the data form and the process, the Department determined whether or not there were a potential violation or whether additional information were required. If the company was determined to be in compliance, they were advised accordingly. If a potential violation were determined or additional information were required, a plant visit was scheduled.

The purpose of the plant visit was to acquire additional information to verify a possible violation or to make a determination of whether or not the company were in violation.

In the case that a violation was verified at the meeting in the department's office, it was felt that this determination should be further substantiated by an inspection of the process. This procedure was followed in order to be certain that a company was in violation of the ordinance prior to requiring the company to take action to remedy the violation.

In some cases, the information obtained at the meeting at the department's office was not sufficient to determine the company's status. In these cases, information obtained during the plant inspection was sufficient to make the necessary determination regarding compliance.

After it was determined that a company was not in compliance with the ordinance, the company was advised of the procedure which provides exemption from the operation of Chapter 17 of the ordinance in order to allow the company time to come into compliance. The effect of this procedure is to allow the company exemption from enforcement action during the time that they are ordering and installing control equipment and/or developing replacement materials.

The procedure consists of the company requesting, in writing, that the Commissioner of the Department of Environmental Control grant a period of grace in which to come into compliance with the applicable section of the ordinance. The information needed to evaluate the request consists of: 1) present status of subject process; 2) proposed methods of remedying the violation; and 3) the time schedule for completing the program.

The present status was usally determined as a result of the previous data. The proposed method was evaluated so the department could determine whether or not the method would have a likelihood of success in the specific case at hand. If the department did not believe that the proposed method had a likelihood of success, the company was advised accordingly. The time schedule was evaluated as to the reasonableness of the time necessary for the particular proposed method. If the compliance program required more than 90 days, the company's case was referred to the Appeal Board of the Department of Environmental Control.

CONCLUDING REMARKS

This paper has presented the Organic Emission Survey Program of the City of Chicago's Department of Environmental Control as a workable and efficient method of bringing about compliance with new legislation. Following the completion of the program, a yearly updating will take place through our established Annual Inspection Program. This will allow for the addition of new companies, the deletion of some old ones, and the annual variations in usage.

As of the writing of this paper, 323 firms have been requested to complete the Organic Emission Data Form. These firms use organic-base solvents in a variety of processes, for example: printing, spray painting, finishing, coating, material treating, dry cleaning, degreasing, and storage. Of the 197 data forms that have been returned and evaluated, 88 percent (174 companies) were found to be in compliance initially. The 23 companies found to be in violation of the hydrocarbon ordinance were placed on control programs: 10 of these companies have completed their programs and are now in compliance. The methods used to achieve compliance included; thermal and/or catalytic incineration; absorption; ultraviolet curing; and reformulation by exempt solvents, water-base material, or high-solids materials. Due to the compliance programs of the above-mentioned 10 companies, 1,611 tons of photochemically reactive material by definition have been abated. The methods being implemented to achieve compliance by the remaining 13 companies are similar to those noted above. When these companies complete their programs we will be able to determine their reductions of pollutants emitted.

The data collected enabled us to update our Emission Inventory. Based on the data evaluated to date, we have determined that the potential solvent emissions are 15.7 percent greater than those given in the previous Emission Inventory.

Accoring to Chapter 17 of the Municipal Code of Chicago, major emitters are required to file and abide by an episode action plan. These plans call for emission reduction when specific pollutant levels are reached in the City and take into account whether or not a company is in compliance with the applicable ordinances. Exhibit 10 presents the criteria of the "Episode Alert Program" of the City of Chicago.

The development and implementation of the Organic Emission Survey Program has been a unique experience for us. In this age of specialization, it is rare that one has the opportunity to maintain such intimate contact with every phase of a program. Being able to deal on a personal basis with most of the surveyed companies has given us insight into many problems which might otherwise, if gone unresolved, have served only to increase the apprehension with which industry deals with regulatory agencies.

This relationship allowed us to efficiently collect our data while requiring only the minimum input by the company.

It is hoped that this paper has communicated what we have learned and incorporated in our program.

ACKNOWLEDGMENT

The authors would like to acknowledge the guidance, interest, and support given to their work by Edward J. Petkus, Director of Engineering, and Don B. Gallay, Assistant Director of Engineering.

APPENDIX

NOTE. - The 10 exhibits called out in text are shown on the following pages.

Exhibit 1

ANALYSIS OF HYDROCARBON AMENDMENT SECTION 17-2 AND PERTINENT DEFINITIONS

AMENDMENTS AS WRITTEN	INTERPRETATION	EXAMPLE
Photochemically Reactive Material: Any organic material with an aggregate of more than 20% of its total volume composed of compounds classified below or the composition of which exceeds any of the following individual percentage, composition limitations: (1) A combination of hydrocarbons, alchohols, aldehydes, esters, ethers or ketones having an olefinic or cyclo-olefinic type of unsaturation: 5%. This definition does not apply to perchloroethylene or trichloroethylene. (2) A combination of aromatic compounds with eight or more carbon atoms to the molecule except ethylbenzene: 8%. (3) A combination of ethylbenzene, ketones having branched hydrocarbon structures or toluene: 20% Whenever any photochemically reactive material or any constituent of any organic material may be classified from its chemical structure (1), (2), (3), it	Photochemically Reactive Material: Any organic material whose composition exceeds 20% by volume of the totaled categories below, or exceeds any of the individual percentages. 1. Olefins or cyclo-olefins - 5% 2. C8 and above - 8% 3. Toluene, ethyl benzene and branched ketones - 20%	The percent of photochemically reactive compound in a formulation is determined in the following manner: Volume of photochemically reactive compound in solvent divided by the volume of organic solids plus the volume of solvent. (See calculations in text.)

Exhibit 1 (con.)

AMENDMENTS AS WRITTEN	INTERPRETATIONS	EXAMPLE
shall be considered as a member of the most reactive group, that is, that group having the least allowable percent of the total organic materials.		
Organic Substance: Any chemical compound of carbon including diluents and thinners which are liquids at standard conditions and which have such uses as dissolvers, viscosity reducers or cleaning agents, but excluding methane, carbon monoxide, carbonic acid, metallic carbonic acid, metallic carbide, metallic carbonates and ammonium carbonate.	Organic Substance: Any compound of carbon (solid liquid or gaseous), along with the inclusions and exclusions stated.	
Volatile Organic Material: Any organic substance which has a vapor pressure of 2.5 pounds per square inch absolute (psia) or greater at 70°F.	Volatile Organic Material As It Differs From Volatile Content: Volatile organic material is defined as an organic substance with a vapor pressure of 2.5 psia at 1 ATM and 70°F; however, in sections 17-2B.7(2)b and 17-2B.7(2)c, the phrase volatile content is used to mean something different. Volatile content is construed to mean liquid phase in those particular sections.	
17-2B.7. No person shall cause or allow the discharge or more than 8 pounds per hour from the use of organic substances into the atmos-	Discharge From Emission Sources: Cannot discharge more than 8 lbs/hr of organic substances into the	A company could emit 8 lbs/hr or less of any organic substance and be in compliance.

Exhibit 1 (con.)

AMENDMENTS AS WRITTEN	INTERPRETATION	EXAMPLE
phere from any emission source except as provided in the following subsections.	atmosphere from any emission source.	
(1) Alternative Standard: Emissions of photochemically reactive material in excess of those permitted in paragraph 17-2B.7 above are allowable if such emissions are controlled by one of the following methods.	EXCEPT 1. More than 8 lbs/hr emission of photochemically reactive material is permissible provided that the emissions are controlled by one of the following:	
(a) flame, thermal or catalytic incineration so as either to reduce such emissions to 10 ppm equivalent methane (molecular weight 16) or less, or to convert 85% of the hydrocarbons to carbon dioxide and water; or	(a) Incineration - must be controlled to 10 ppm calculated as methane or to 85% efficiency.	(a) A company has the option to reduce emissions by incineration 85% or to 10 ppm calculated as methane. This would mean that for concentrations of 66 ppm (Calculated as methane) or less, control device of less than 85% efficiency would be adequate. Because this could bring the ppm calculated as methane below 10.
(b) a vapor recovery system which which absorbs and/or condenses at least 85% of the total uncontrolled organic substance that would be otherwise emitted to the atmosphere; or	(b) Vapor recovery system - must be at least 85% efficient.	
(c) any other pollution control equipment approved by the Commissioner capable of reducing by 85% or more the uncontrolled organic substance that	(c) Any other approved device - must be 85% efficiency.	

Exhibit 1 (con.)

would be otherwise emitted to the atmosphere.		
(2) Exceptions: The provisions of this paragraph 17-2B.7 shall not apply to the following:	(2) Exceptions: 8 lb/hr limitation does not apply to:	2b. A company using a formulation, classified as photochemically reactive, composed of a solid phase, and a liquid phase consisting of only water and organics, could emit greater than 8 lb. and be in compliance provided that the organics comprise 30% or less of the liquid phase.
(a) The spraying or use of insecticides, herbicides, or other pesticides. (b) To the use of any substance in any article, process, or machine equipment, or device if: (i) the volatile content of such substance consists only of water and organic substances; and (ii) the organic substance comprises not more than 30% of said volatile content.	a. Spraying or use of insecticides, herbicides or pesticides. b. The use of substances whose liquid phase is comprised only of water and organics. The organic portion does not exceed 30% by volume of the liquid phase.	
(c) To the use of any substance in any article process, or machine, equipment or device if the volatile content of such substance does not exceed 30% by volume of said substance.	c. The use of substances whose liquid phase does not exceed 30% by volume, of the substance.	2c. A company can discharge in excess of 8 lb/hr of a material classified as photochemically reactive provided that the material's liquid phase comprises not more than 30% of the total volume.
(d) The transport and application of paving asphalt and paving marking paint.	d. Transport and application of paving asphalt and and paving marking paint.	
(3) Further Exceptions: If no odor nuisance exists, this paragraph 17-2B.7 shall apply only to photochemically reactive material.	(3) Further Exceptions: If no odor nuisance exists, the 8 lb/hr limitation applies only to photochemically reactive material except #1 and #2.	3. If there is no odor nuisance the company can emit an unlimited amount of material that is classified non-photochemically reactive, but to 8 lb/hr of reactive material unless exemption #1 or #2 is met.

Exhibit 2

CITY OF CHICAGO
DEPARTMENT OF ENVIRONMENTAL CONTROL

RICHARD J. DALEY
MAYOR

H. W. POSTON
COMMISSIONER

XYZ Company
123 1st St.
Chicago, Ill. 60600

Attn: Mr. J. Jones, President

Gentlemen:

On May 29, 1974, the City Council for the City of Chicago adopted a new hydrocarbon amendment to Chapter 17 of the Municipal Code which became effective on June 8, 1974.

You are required to complete the enclosed data so that this department can determine whether or not your emission sources are in compliance. Your response should be forwarded to the attention of Messrs George Czerniak or William T. Thorp within thirty (30) days from the date of this letter.

Your cooperation in this matter is appreciated.

Sincerely yours,

Edward J. Petkus
Director of Engineering

Enclosure

320 North Clark Street Chicago, Illinois 60610 Phone Area Code 312 744-4070

Exhibit 3 - Attachment

Article IIC

CONTROL OF EMISSIONS OF ORGANIC SUBSTANCES

Definitions

17-2C.1. For the purpose of this Article, whenever any of the following words, terms or definitions are used herein, they shall have the meaning ascribed to them in this Section.

Air Contaminant: Any smoke, soot, fly ash, dust, cinders, dirt, noxious or obnoxious acids, fumes, oxides, gases, vapors, odors, toxic or radioactive substances, waste, particulate, solid, liquid or gaseous matter, or any other materials in such place, manner or concentration as to cause injury, detriment, nuisance, or annoyance to the public, or to endanger the health, safety or welfare of the public, or as to cause or have a tendency to cause injury or damage to business or property.

Architectural Coating: Any coating used for residential, commercial or industrial buildings and their appurtenances, that is on site applied.

Conservation Vent Valve: A weight-loaded valve designed and used to reduce evaporation losses of volatile organic substances by limiting the amount of air admitted to, or vapors released from the vapor space of a closed storage vessel.

Control Apparatus: Any device which prevents, eliminates, or controls the emission of any air contaminant.

Equipment: Any device capable of causing the emission of an air contaminant into the open air, and any stack, chimney, conduit, flue, duct, vent or similar device connected or attached or serving the equipment. This shall include equipment in which the preponderance of the air contaminants emitted is caused by a manufacturing process.

Floating Roof: A storage vessel cover consisting of a double deck, pontoon single deck, internal floating cover or covered floating roof, which rests upon and is supported by the liquid content being contained, and is equipped with a closure seal or seals to close the space between the roof edge and tank wall.

Manufacturing Process: Any action, operation or treatment embracing chemical, industrial manufacturing, or processing factors, methods or forms including, but not limited to, furnaces, kettles, ovens, converters, cupolas, kilns, crucibles, stills, dryers, roasters, crushers, grinders, mixers, reactors, regenerators, separators, filters, reboilers, columns, classifiers, screens, quenchers, cookers, digesters, towers, washers, scrubbers, mills, condensers or absorbers.

Maximum Allowable Emission Rate: The maximum amount of an air contaminant which may be emitted into the outdoor air during any prescribed interval of time.

Odor Nuisance: Any noxious odor in sufficient quantities and of such characteristics and duration as to be injurious to human, plant, or animal life, to health, or to property, or to unreasonably interfere with the enjoyment of life or property.

Oil-Effluent Water Separator: Any tank, box sump, or other container or group of such containers in which any organic material floating on, or entrained, or contained in water entering such containers is physically separated and removed from such water prior to the exit from the container of such water.

Organic Substance: Any chemical compound of carbon including diluents and thinners which are liquids at standard conditions and which have such uses as dissolvers, viscosity reducers or cleaning agents, but excluding methane, carbon monoxide, carbon dioxide, carbonic acid, metallic carbonic acid, metallic carbide, metallic carbonates and ammonium carbonate.

Organic Vapor: Gaseous phase of an organic substance or a mixture of organic substances present in the atmosphere.

Exhibit 3 - Attachment (con.)

Particulate Matter: Any solid or liquid material, other than water, which exists in finely divided form.

Petroleum Liquids: Any crude petroleum, condensate, and any finished or intermediate products manufactured in a petroleum refinery but does not mean Number 2 through Number 6 fuel oils as specified in ASTM-D-396-69, gas turbine fuel oils Numbers 2-GT through 4-GT as specified in ASTM-D-2880-71, or diesel fuel oils Numbers 2-D and 4-D as specified in ASTM-D-975-68.

Photochemically Reactive Material: Any organic material with an aggregate of more than 20 percent of its total volume composed of the chemical compounds classified below or the composition of which exceeds any of the following individual percentage, composition limitations:

(1) A combination of hydrocarbons, alcohols, aldehydes, esters, ethers or ketones having an olefinic or cycloolefinic type of unsaturation: 5 percent. This definition does not apply to perchloroethylene or trichloroethylene.
(2) A combination of aromatic compounds with eight or more carbon atoms to the molecule except ethylbenzene: 8 percent.
(3) A combination of ethylbenzene, ketones having branched hydrocarbon structures or toluene: 20 percent.

Whenever any photochemically reactive material or any constituent of any organic material may be classified from its chemical structure (1), (2), (3), it shall be considered as a member of the most reactive group, that is, that group having the least allowable percent of the total organic materials.

Pressure Tank: A tank in which fluids are stored at a pressure greater than atmospheric pressure.

Stack or Chimney: A flue, conduit or opening designed and constructed for the purpose of emitting air contaminants into the outdoor air.

Standard Conditions: Shall be 70°F. and one atmosphere pressure (14.7 psia or 760 mm Hg).

True Vapor Pressure: The equilibrium partial pressure exerted by a petroleum liquid as determined in accordance with methods described in American Petroleum Institute Bulletin 2517, Evaporation Loss From Floating Roof Tanks, 1962.

Volatile Organic Material: Any organic substance which has a vapor pressure of 2.5 pounds per square inch absolute (psia) or greater at 70°F.

Emissions from Large Tanks

17-2C.2A. No person shall cause or allow the storage of any volatile organic material in any stationary tank, reservoir or other container of more than 40,000 gallons capacity unless such tank, reservoir or other container:

(1) is a pressure tank capable of withstanding the vapor pressure of such materials, so as to prevent vapor or gas loss to the atmosphere at all times; or

(2) is designed and equipped with one of the following vapor loss control devices:

  (a) a floating roof which rests on the surface of the volatile organic material and is equipped with a closure seal or seals to close the space between the roof edge and the tank wall. Such floating roof shall not be permitted if the volatile organic material has a vapor pressure of 12.5 pounds per square inch absolute or greater at 70°F. No person shall cause or allow the emission of air contaminants into the atmosphere from any gauging or sampling devices attached to such tanks, except during sampling.

  (b) a vapor recovery system consisting of:

    (i) a vapor gathering system capable of collecting 90% or more of the uncontrolled volatile organic material that would be otherwise emitted to the atmosphere; and

    (ii) a vapor disposal system capable of processing such volatile organic material so as to prevent their emission to the atmosphere. No person shall cause or allow the emission of air contaminants into the atmosphere from any gauging or sampling devices attached to such tank, reservoir or other container except during sampling.

  (c) other equipment or means of equal efficiency approved by the Commissioner.

(3) is an existing cone roof tank used exclusively for the storage of Illinois crude oil, if all the following conditions are met:

(a) the vapor pressure of such crude oil is less than 5 pounds per square inch absolute (psia); and,

(b) the location of such tank is outside a major metropolitan area; and,

(c) such tank is equipped with positive pressure tank vent valves and vacuum breakers.

Petroleum Liquid Storage

17-2C.2B. The owner or operator of any new storage vessel for petroleum liquids which has a storage capacity of greater than 40,000 gallons shall store petroleum liquids as follows:

(1) If the true vapor pressure of the petroleum liquid, as stored, is equal to or greater than 78 mm Hg (1.5 psia) but not greater than 570 mm Hg (11.1 psia), the storage vessel shall be equipped with a floating roof, a vapor recovery system, or their equivalents.

(2) If the true vapor pressure of the petroleum liquid as stored is greater than 570 mm Hg (11.1 psia), the storage vessel shall be equipped with a vapor recovery system or its equivalent.

Loading Facilities

17-2C.3. (1) No person shall cause or allow the discharge of more than 8 pounds per hour of volatile organic material into the atmosphere during the loading of any volatile organic material from the aggregate loading pipes of any loading facility having a throughput of greater than 40,000 gallons per day into any railroad tank car, tank truck or trailer unless such loading facility is equipped with submerged loading pipes or a device that is equally effective in controlling emissions and is approved by the Commissioner according to the provisions of this Ordinance.

(2) No person shall cause or allow the loading of any volatile organic material into any stationary tank having a storage capacity of greater than 250 gallons, unless such tank is equipped with a permanent submerged loading pipe or an equivalent device approved by the Commissioner according to the provisions of Article I of this Chapter, or unless such tank is a pressure tank or is fitted with a recovery system as described in Section 17-2C.2A(2)(b).

(a) Exception: This Subparagraph 17-2C.3(2) shall not apply to: (1) the loading of such volatile organic substances into any tank having a capacity of less than 2,000 gallons which was installed underground or below street-grade level prior to the date of the adoption of this rule, and (2) in-plant tanks used exclusively for blending, mixing or weighing.

Water Separator

17-2C.4. No person shall use any single- or multiple-compartment effluent water separator which receives effluent water containing 200 gallons a day or more of organic substance from any equipment processing, refining, treating, sorting, or handling organic substance unless such effluent water separator is equipped with air pollution control equipment capable of reducing by 85 percent or more the uncontrolled organic substance emitted to the atmosphere.

Exception: If no odor nuisance exists, this Paragraph 17-2C.4 shall apply only to volatile organic material.

Pump or Compressor Volatiles

17-2C.5. No person shall cause or allow the discharge of more than two cubic inches of liquid volatile organic materials into the atmosphere from any pump or compressor in any 15 minute period at standard conditions.

Architectural Coatings

17-2C.6. No person shall cause or allow the sale or use in the City of Chicago of any architectural coating containing more than 20 percent by volume of photochemically reactive material in containers having a capacity of more than one gallon.

No person shall thin or dilute any architectural coating for use in the City of Chicago with a solvent containing a photochemically reactive material in quantity greater than one quart of solvent per gallon of architectural coating.

Exhibit 3 - Attachment (con.)

Exceptions

17-2C.7. No person shall cause or allow the discharge of more than 8 pounds per hour from the use of organic substances into the atmosphere from any emission source except as provided in the following subsections:

(1) **Alternative Standard:** Emissions of photochemically reactive material in excess of those permitted in Paragraph 17-2C.7 above are allowable if such emissions are controlled by one of the following methods:

- (a) flame, thermal or catalytic incineration so as either to reduce such emissions to 10 ppm equivalent methane (molecular weight 16) or less, or to convert 85 percent of the hydrocarbons to carbon dioxide and water; or
- (b) a vapor recovery system which absorbs and/or condenses at least 85 percent of the total uncontrolled organic substance that would be otherwise emitted to the atmosphere; or
- (c) any other pollution control equipment approved by the Commissioner capable of reducing by 85 percent or more the uncontrolled organic substance that would be otherwise emitted to the atmosphere.

(2) **Exceptions:** The provisions of this Paragraph 17-2C.7 shall not apply to the following:

- (a) The spraying or use of insecticides, herbicides, or other pesticides.
- (b) To the use of any substance in any article, process, or machine, equipment, or device if
  - (i) the volatile content of such substance consists only of water and organic substances; and
  - (ii) the organic substances comprise not more than 20 percent of said volatile content.
- (c) To the use of any substance in any article, process, or machine, equipment or device if the volatile content of such substance does not exceed 20 percent by volume of said substance.
- (d) The transport and application of paving asphalt and paving marking paint.

(3) **Further Exceptions:** If no odor nuisance exists, this Paragraph 17-2C.7 shall apply only to photochemically reactive material.

Odors

17-2C.8. No person shall cause, suffer, allow or permit to be emitted into the outdoor air volatile organic material which will result in odors detectable by sense of smell in any area of public use or occupancy off the premises, and which constitute an odor nuisance, as defined in 17-2C.1, notwithstanding compliance with the requirements of other Sections of this Chapter.

Exception: Inedible rendering plants as defined in 17-2D.1 and covered in 17-2D.2.

Measurement

17-2C.9. The total organic substance concentrations in an effluent stream shall be measured by a Flame Ionization Detector, or by other methods approved by the Commissioner.

Petroleum Refinery and Petrochemical Manufacturing Process Emissions

17-2C.10. No person shall cause or allow the discharge of organic substance in the atmosphere from:

- (a) Any catalyst regenerator of a petroleum cracking system; or
- (b) Any petroleum fluid coker; or
- (c) Any other waste gas stream from any petroleum or petrochemical manufacturing process; in excess of 100 ppm equivalent methane (molecular weight 16.0).

Vapor Blowdown

17-2C.11. No person shall cause or allow the emission of organic substance into the atmosphere from any vapor blowdown system or any safety relief valve, except such safety relief valves not capable of causing an excessive release, unless such emission is controlled —

- (a) To 10 ppm equivalent methane (molecular weight 16.0) or less; or
- (b) By combustion in a smokeless flare, or
- (c) By other air pollution control equipment approved by the Commissioner.

Exhibit 3 - Attachment (con.)

Safety Relief Valves

17-2C.12. **Sets of Unregulated Safety Relief Valves Capable of Causing Excessive Releases.** Section 17-2C.11 shall not apply to any set of unregulated safety relief valves capable of causing excessive releases, provided that the owner or operator thereof, by the effective date of the ordinance, provides the Commissioner with the following:

(a) A historical record of each such set (or, if such records are unavailable, of similar sets which, by virtue of operation under similar circumstances, may reasonably be presumed to have the same or greater frequency of excessive releases) for a three-year period immediately preceding the effective date of the ordinance, indicating:

  (1) Dates on which excessive releases occurred from each such set; and

  (2) Duration in minutes of each such excessive release; and

  (3) Quantities (in pounds) of mercaptans and/or hydrogen sulfide emitted into the atmosphere during each such excessive release;

(b) Proof, using such three-year historical records, that no excessive release is likely to occur from any such set either alone or in combination with such excessive releases from other sets owned or operated by the same person and located within a ten mile radius from the center point of any such set, more frequently than 3 times in any 12 month period; and

(c) Accurate maintenance records pursuant to the requirements of Paragraph 17-2C.12(a) of this Section; and

(d) Proof, at three-year intervals, using such three-year historical records, that such set conforms to the requirements of Paragraph 17-2C.12(c) of this Section.

Clean-up Operations

17-2C.13. Emissions of organic material released during clean-up operations and disposal shall be included with other emissions of organic substance from the related emission source or air pollution control equipment in determining total emissions.

Disposal of More Than Five Gallons

17-2C.14. No person shall during any one day discard a total of more than 5 gallons of any volatile organic substance by any means which will permit evaporation of such substance into the atmosphere.

Effective Date

17-2C.15. Every owner or operator of a new emission source, the plans for which are 80% or less completed by the effective date of this Chapter, shall comply with the standards and limitations on the effective date of this Chapter.

Every owner or operator of an existing emission source shall comply with the standards and limitations within 90 days of the effective date of this Chapter.

Submerged Loading Pipe: Any loading pipe the discharge opening of which is entirely submerged when the liquid level is six inches above the bottom of the tank. When applied to a tank which is loaded from the side, any loading pipe the discharge of which is entirely submerged when the liquid level is 18 inches or two times the loading pipe diameter, whichever is greater, above the bottom of the tank. This definition shall also apply to any loading pipe which is continuously submerged during loading operations.

EXHIBIT 3 - PAGE 1 of FORM

ORGANIC EMISSION DATA FORM

(formerly "Hydrocarbon Data Form")

Please complete this form to the best of your ability. The information required to complete this form should be readily available from either your suppliers or your knowledge of plant equipment and operations. You are not required to perform any calculations or testing in order to complete this form.

This form consists of three sections concerning your plant operations. Also included on pages 13, 14 and 15 is a copy of Chapter 17, Article II C of Municipal Code of Chicago and a working definition of a submerged loading pipe.

If you require any assistance in the completion of this form, call either George Czemiak, William Thorp or Philip Byron at (312) 744-3118.

GENERAL DATA

COMPANY NAME: ADDRESS: (ZIP CODE)

TELEPHONE: DATE:

NAME OF PERSON RESPONSIBLE FOR SECTION:	TITLE:	SIGNATURE:
I		
II		
III		

(Form #2, Jan 10, 1975)

SECTION I (Exhibit 3 Page 2 of Form)

Instructions for completing Section I.

Complete this section if you use one or more stationary tanks with a capacity of greater than 250 gallons, otherwise mark non-applicable.

Complete one column on Table I for each tank.

The information requested in part A should be available from your supplier.

The information requested in parts B and C should be available upon inspection or from plant records.

For each tank enter the following information (parts A, B, and C) in the provided spaces on the following pages:

A1 Organic Stored - Enter either the trade name or chemical name of each organic stored.

A2 Petroleum Liquid - Check if organic stored is a petroleum liquid. (Includes gasoline).

A3 Vapor Pressure - Enter the vapor pressure of each organic in units of PSIA at 70°F. If the organic is a petroleum liquid, enter the true vapor pressure of the liquid as determined in accordance with methods described in American Petroleum Institute Bulletin 2517.

B1 Capacity of Container - Enter the container capacity in units of gallons.

B2 Above - Below Grade - State whether the storage container is above or below grade.

B3 Outdoors - Check column if storage container is outdoors.

B4 Pressure Rating - If storage tank is a pressure tank, enter pressure rating.

B5 Submerged Loading Pipes (note the working definition of submerged loading pipes before completing this part, see page 15). - Check if storage tank is equipped with permanent submerged loading pipes.

B6 Installed Since 6/74 - Check if storage container was installed since 6/74.

B7 Mix, Blend, or Weight - Is this an in plant tank used exclusively for mixing, blending or weighing (state yes or no).

C1 Control Device - Describe any vapor loss control device.

C2 Use - Describe the use of the stored organic (fuel, thinner, etc.).

C3 Sketch - Roughly sketch and label each storage system, including tank, loading pipes, control device. Sketch on Page No. 4.

SECTION I - TABLE I (Exhibit 3 Page 3 of Form)

A1 Organic Stored							
A2 Petroleum Liquid							
A3 Vapor Pressure							
B1 Capacity of Container							
B2 Above - Below Grade							
B3 Outdoors							
B4 Pressure Rating							
B5 Submerged Loading Pipes							
B6 Installed Since 6/74							
B7 Mix, Blend or Weigh							
C1 Control Device							
C2 Use							

[ED. NOTE: Page 4 of this form is blank.]

SECTION I C-3 (Exhibit 3 Page 4 of Form)

(Exhibit 3 Page 5 of Form)

SECTION II

Instructions for completing Section II.

Complete this section if you use one or more liquid compounds in a process.

Section II A relates to the compound used in the process. Section II B relates to material used to thin the compounds given in Section II A.

Complete one column on Table II A for each liquid compound used in a process. This information is to be based on the compound as delivered from the manufacturer. If you thin the compound, then complete Section II B. Section II A contains an explanation of the information requested in Table II A.

If you use a large number of compounds (20 or 50) please give us a call for assistance.

If you are required to complete Section II B, complete one row of Table II B for each thinner used. This information is to be based on the thinner as delivered from the manufacturer. The information for each thinner need be listed only once on Table II B. Section II B contains an explanation of the information requested in Table II B.

If you require additional space on either Table II A or Table II B make a copy of the table and enter the additional information on the copy. On the original table indicate the number of added table copies.

The information requested in Table II A, 2a thru 3c (inclusive) and 8a thru 10b (inclusive) should be available from your plant records, all other information requested in Table II A should be available from your supplier.

All of the information requested in Table II B, except 3, should be available from your supplier.

(Exhibit 3 Page 6 of Form)

SECTION II A

Explanation of the information requested in Table II A.

1a. Formulation Used - Enter trade name and/or identification number of liquid compound used.

1b. Photo Reactive - To the best of your knowledge is the formulation photochemically reactive as defined in Chapter 17-2C.1 of the Municipal Code of Chicago. (See page 13 of this form). State yes or no.

2a. Avg Gal/Day - Enter the average number of gallons per day used in the process.

2b. Days/Year - Enter the number of days per year that the process using this formulation is in operation.

2c. Hours/Day - Enter the number of working hours per day for the process using this formulation (this number is not to include down time).

3a. Max Gal/Day - Enter the maximum number of gallons of formulation used per day in the process.

3b. Days/Year - Enter the number of days per year that the maximum amount of formulation is used.

3c. Hours/Day - Enter the number of working hours per day for the process when using the maximum amount of the formulation (this number is not to include down time).

4. Weight/Gal - Enter the weight per gallon of the formulation (lbs.).

5a. Volume % Solids - Enter the volume percent of the formulation which is comprised of solid material.

5b. Weight % Solids - Enter the weight % of the formulation which is comprised of solid material.

5c. Volume % Solids Organic - Enter the volume percent of the solid portion of the formulation which is comprised of organic material.

(Exhibit 3 Page 7 of Form)

6a. Volume % Organic Solvent - Enter the volume percent of the formulation which is comprised of organic solvent.

6b. Weight % Organic Solvent - Enter the weight percent of the formulation which is comprised of organic solvent.

6c. Volume % Class (1) Compounds - Enter the volume percent of the organic solvent portion which is comprised of material classified in (1) of the definition of "Photochemically Reactive Material" given on page 13 of this form.

6d. Volume % Class (2) Compounds - Enter the volume percent of the organic solvent portion which is comprised of material classified in (2) of the definition of "Photochemically Reactive Material" given on page 13 of this form.

6e. Volume % Class (3) Compounds - Enter the volume percent of the organic solvent portion which is comprised of material classified in (3) of the definition of "Photochemically Reactive Material" given on page 13 of this form.

7a. Name of Other - If applicable, enter the name of other material (besides solids and organic solvent) which is used to make up the formulation.

7b. Weight % of Other - Enter the weight percent of the formulation which is comprised of other material.

7c. Volume % of Other - Enter the volume percent of the formulation which is comprised of other material.

8a. Process - Describe the process in which the formulation is used; ie printing, painting, cleanup, etc.

8b. Control Device - Describe any control device used in conjunction with the process. If stack test results are available, these should be submitted.

(Exhibit 3 Page 8 of Form)

9a. Thinner #1 - If the formulation, as delivered from the manufacturer, is thinned at your plant, enter the name of the thinner in column 9a. If two thinners are used, enter the name of the second thinner in column 10a. If more than two thinners are used prepare an addendum to this form in which the names of the additional thinners for this formulation are labeled 11a, 12a, etc. as required. (Also include in the addendum 11b, 12b, giving the respective thinner rate).

9b. Thinner Rate #1 - Enter the number of gallons of thinner #1 used per gallon of the formulation.

10a. Thinner #2 - Enter the name of the second thinner (if used).

10b. Thinner Rate #2 - Enter the number of gallons of thinner #2 used per gallon of the formulation.

SECTION II A (Exhibit 3 Page 9 of Form)

TABLE II A

1a	Formulation Used				
1b	Photo Reactive				
2a	Avg. Gal/Day				
2b	Days/Year				
2c	Hours/Day				
3a	Max. Gal/Day				
3b	Days/Year				
3c	Hours/Day				
4	Weight/Gal				
5a	Volume % Solids				
5b	Weight % Solids				
5c	Volume % Solids Organic				
6a	Volume % Organic Solvent				
6b	Weight % Organic Solvent				
6c	Volume % Class (1) Compounds				
6d	Volume % Class (2) Compounds				
6e	Volume % Class (3) Compounds				
7a	Name of Other				
7b	Weight % of Other				
7c	Volume % of Other				
8a	Process				
8b	Control Device				
9a	Thinner #1				
9b	Thinner Rate #1				
10a	Thinner #2				
10b	Thinner Rate #2				

(Exhibit 3 Page 10 of Form)

SECTION II B

Explanation of the information requested in Table II B.

1a Name of Thinner - Enter the trade name and/or identification number of the liquid compound used.

1b Photo Reactive - To the best of your knowledge is the compound photochemically reactive as defined in Chapter 17-2C.1 of the Municipal Code of Chicago. (See page 13 of this form). State yes or no.

2. Weight/Gal - Enter the weight per gallon of the formulation (lbs.).

3. Gal/Day - Enter the average number of gallons per day used.

4a. Volume % Class (1) Compound - Enter the volume percent of the thinner which is comprised of material classified in (1) of the definition of "Photochemically Reactive Material" given on page 13 of this form.

4b. Volume % Class (2) Compound - Enter the volume percent of the thinner which is comprised of material classified in (2) of the definition of "Photochemically Reactive Material" given on page 13 of this form.

4c. Volume % Class (3) Compound - Enter the volume percent of the thinner which is comprised of material classified in (3) of the definition of "Photochemically Reactive Material" given on page 13 of this form.

SECTION II B

TABLE II B

(Exhibit 3 Page 11 of Form)

(1a) Name of Thinner	(1b) Photo Reactive	(2) Weight Gal	(3) Gal Day	(4a) Volume % Class (1) Compound	(4b) Volume % Class (2) Compound	(4c) Volume % Class (3) Compoun

(Exhibit 3 Page 12 of Form)

SECTION III

Answer the following questions yes or no.

A. Do you load more than 40,000 gallons per day of organic material into railroad tank cars, tank trucks or trailers? ________

B. Do you use a single or multiple compartment effluent water separator? ________

C. Is there a vapor blowdown system or a safety release valve associated with your plant? ________

D. Do you presently have or are you requesting a compliance program or a variance with the State of Illinois for hydrocarbon emissions? ____________
(If your answer is yes, include a status report and a copy of relevant material, such as the order of the Pollution Control Board, petitions, compliance plan, etc.)

NOTE: Due to the format specifications of this paper, pages 13 thru 15 of the "Organic Emission Data Form" have been replaced with the following 5 pages.

Exhibit 4

CITY OF CHICAGO
DEPARTMENT OF ENVIRONMENTAL CONTROL

RICHARD J. DALEY
MAYOR

H. W. POSTON
COMMISSIONER

XYZ Company
123 1st St.
Chicago, Ill. 60600

Attn: Mr. J. Jones, President

Gentlemen:

In October, 1974, your firm was sent information and guidance pertaining to the new hydrocarbon amendment of the City ordinance.

At that time you were requested to fill out the attached data sheets. It has come to our attention that additional time may be required in the preparation of these data sheets.

If your company requires any assistance or a time extension, please feel free to call Messrs George Czerniak, William Thorp or Philip Byron at 744-3118 or 3119.

Sincerely,

Edward J. Petkus
Director of Engineering

320 North Clark Street Chicago, Illinois 60610 Phone Area Code 312 744-4070

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Exhibit 5

CITY OF CHICAGO
DEPARTMENT OF ENVIRONMENTAL CONTROL

RICHARD J. DALEY
MAYOR

H. W. POSTON
COMMISSIONER

XYZ Company
123 1st St.
Chicago, Ill. 60600

Attn: Mr. J. Jones, President

Dear Sir:

Your firm was notified on October 17, 1974, and November 25, 1974, of the necessity to complete certain hydrocarbon data sheets so that a determination could be made as to your emission sources compliance.

To date, your firm has not complied with these requests, therefore, if the referenced forms are not on file with this department by January 17, 1975, enforcement action will be taken.

Very truly yours,

Edward J. Petkus
Director of Engineering

cc: Enforcement Division
Corporation Counsel

320 North Clark Street Chicago, Illinois 60610 Phone Area Code 312 744-4070

Printed on 100% Recycled Paper

Exhibit 6

HYDROCARBON COMPLIANCE SUMMARY

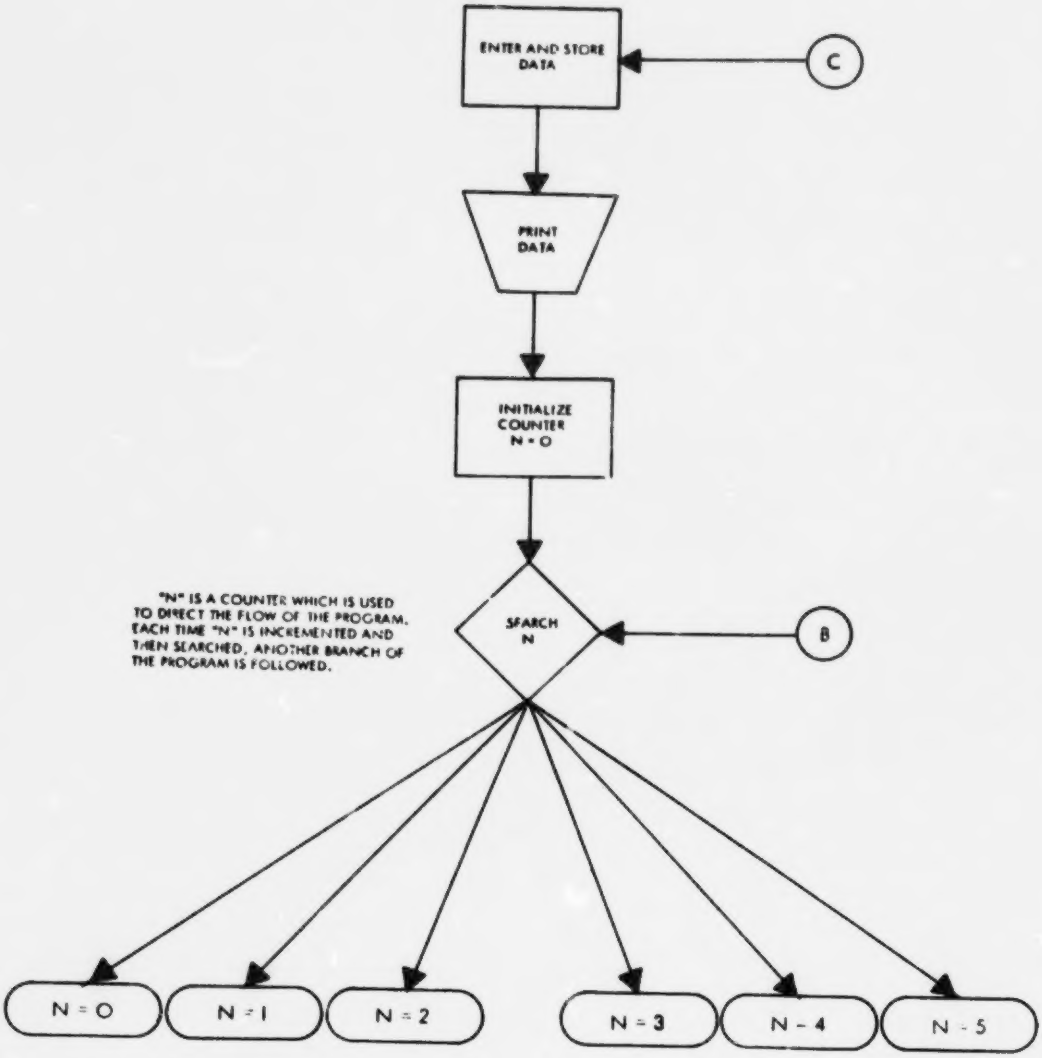
COMPANY NAME: XYZ CO.

	FORMULATION # 1	2	3
AVG. GAL/DAY	6.00	3.00	8.00
HRS./DAY	8.00	8.00	10.00
MAX. GAL/DAY	9.00	6.00	16.00
HRS./DAY	8.00	8.00	10.00
WT./GAL	8.00	7.40	20.00
VOL. % SOLIDS	.14	.11	.80
VOL. % SOLIDS ORGANIC	.66	.80	.00
WT. % ORGANIC SOLVENT	.76	.80	.15
VOL. % CLASS 1	.00	.09	.00
VOL. % CLASS 2	.01	.00	.00
VOL. % CLASS 3	.49	.00	.00
NAME OF OTHER	.00	.00	.00
VOL. % OTHER	.00	.00	.00
THINNER RATE #1	1.00	1.00	.00
THINNER RATE #2	.00	.00	.00
CONTROL EFFICIENCY	.00	.00	.00
THIN. #1 WT./GAL	6.86	6.86	.00
THIN. #1 GAL./DAY	6.00	3.00	.00
THIN. #1 VOL. % CLASS 1	.00	.00	.00
THIN. #1 VOL. % CLASS 2	.00	.00	.00
THIN. #1 VOL. % CLASS 3	.19	.19	.00
THIN. #2 WT./GAL	.00	.00	.00
THIN. #2 GAL./DAY	.00	.00	.00
THIN. #2 VOL. % CLASS 1	.00	.00	.00
THIN. #2 VOL. % CLASS 2	.00	.00	.00
THIN. #2 VOL. % CLASS 3	.00	.00	.00

	COAT-ING REAC.	THINNER 1 REACTIVE	THINNER 2 REACTIVE	FORMU-LATION REACTIVE	OTHER EXEMP-TION	AVG. LB/HR	MAX. LB/HR
FORMULATION # 1	YES	NO	N/A	YES	NONE	9.68	14.52
FORMULATION # 2	YES	NO	N/A	NO	NONE	4.78	9.56
FORMULATION # 3	NO	N/A	N/A	NO	HI SOL	2.40	4.80

Exhibit 7

HYDROCARBON COMPLIANCE SUMMARY
FLOW DIAGRAM


ENTER AND STORE DATA
C
PRINT DATA
INITIALIZE COUNTER N = O
SEARCH N
B
N = O
N = 1
N = 2
N = 3
N – 4
N = 5

"N" IS A COUNTER WHICH IS USED TO DIRECT THE FLOW OF THE PROGRAM. EACH TIME "N" IS INCREMENTED AND THEN SEARCHED, ANOTHER BRANCH OF THE PROGRAM IS FOLLOWED.

Exhibit 7 (con.)

HYDROCARBON COMPLIANCE SUMMARY
FLOW DIAGRAM

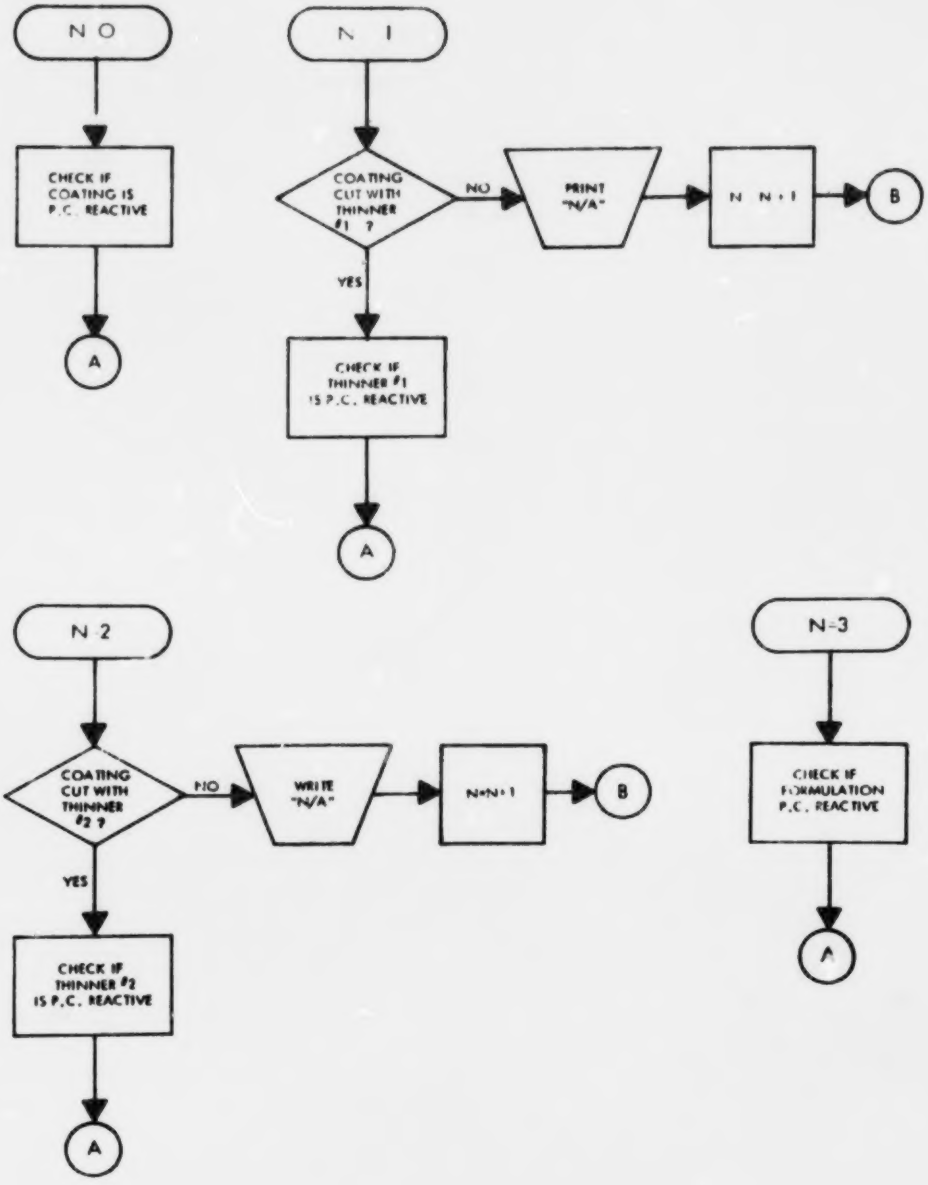

N 0
CHECK IF COATING IS P.C. REACTIVE
A
N 1
COATING CUT WITH THINNER #1 ?
NO
PRINT "N/A"
N N+1
B
YES
CHECK IF THINNER #1 IS P.C. REACTIVE
A
N-2
COATING CUT WITH THINNER #2 ?
NO
WRITE "N/A"
N=N+1
B
YES
CHECK IF THINNER #2 IS P.C. REACTIVE
A
N-3
CHECK IF FORMULATION P.C. REACTIVE
A

Exhibit 7 (con.)

HYDROCARBON COMPLIANCE SUMMARY
FLOW DIAGRAM

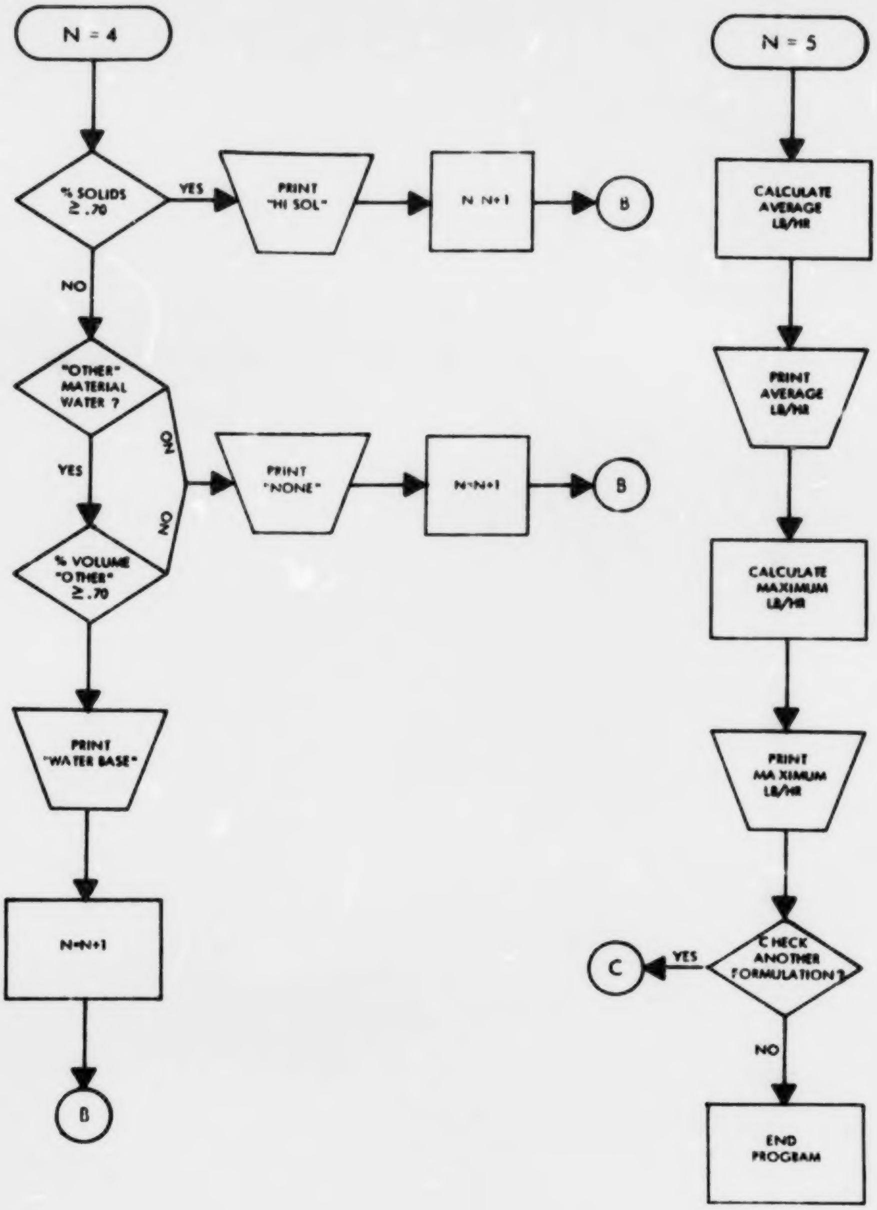

N = 4
% SOLIDS ≥ .70
YES
PRINT "HI SOL"
N=N+1
B
NO
"OTHER" MATERIAL WATER ?
NO
YES
PRINT "NONE"
N=N+1
B
NO
% VOLUME "OTHER" ≥ .70
PRINT "WATER BASE"
N=N+1
B
N = 5
CALCULATE AVERAGE LB/HR
PRINT AVERAGE LB/HR
CALCULATE MAXIMUM LB/HR
PRINT MAXIMUM LB/HR
CHECK ANOTHER FORMULATION?
YES
C
NO
END PROGRAM

Exhibit 7 (con.)

HYDROCARBON COMPLIANCE SUMMARY
FLOW DIAGRAM

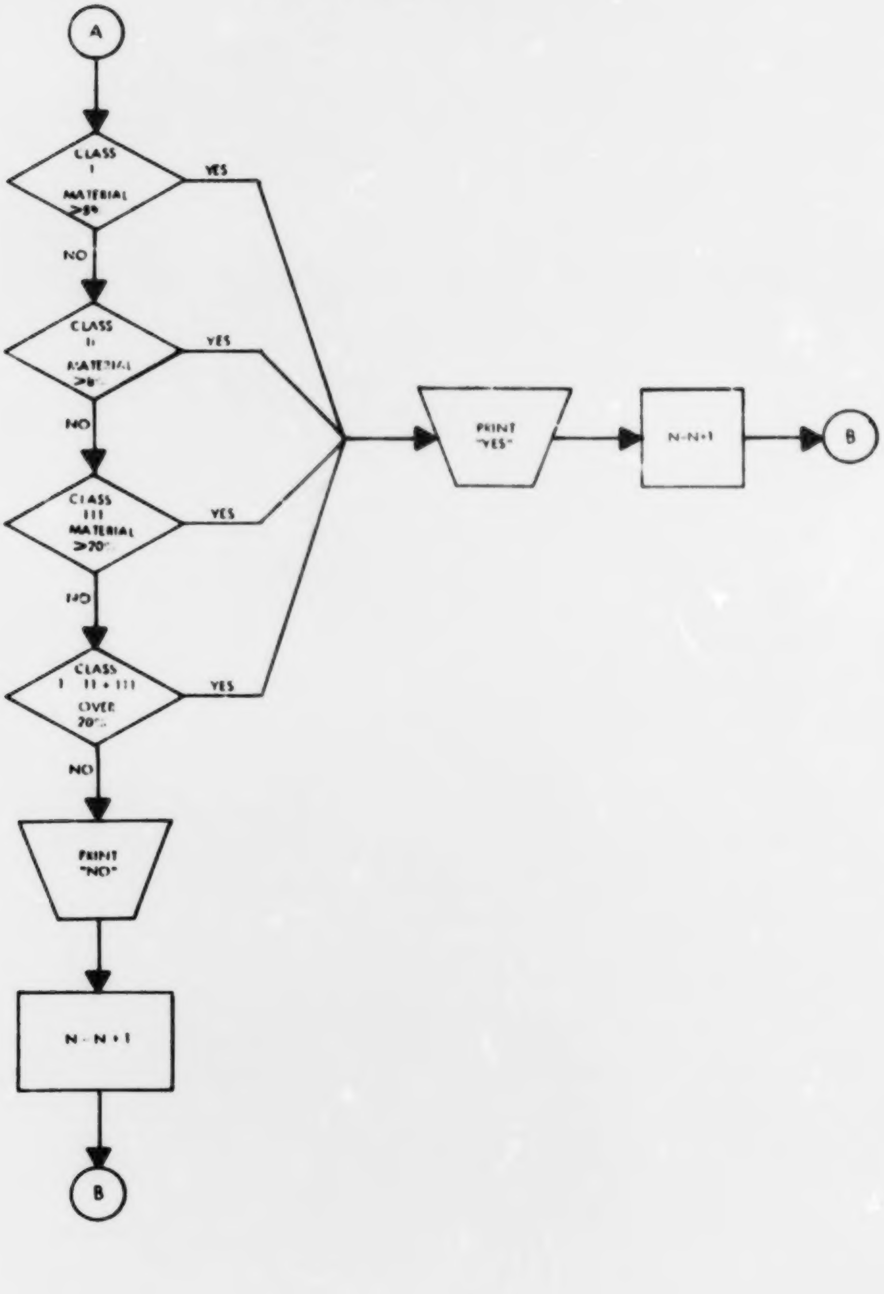

A
CLASS I MATERIAL >5%
YES
NO
CLASS II MATERIAL >8%
YES
NO
CLASS III MATERIAL >20%
YES
NO
CLASS I, II + III OVER 20%
YES
NO
PRINT "YES"
N=N+1
B
PRINT "NO"
N=N+1
B

Exhibit 8

HYDROCARBON DATA SUMMARY

COMPANY: ______________________________ DATE: __________

FORMULATION NO.

	1	2	3	4	5
1. PHOTO-CHEM REACTIVE BY DEF.	1.	1.	1.	1.	1.
2. AVG. GAL/DAY	2.	2.	2.	2.	2.
3. DAYS/YEAR	3.	3.	3.	3.	3.
4. VOL. % SOLVENT	4.	4.	4.	4.	4.
5. VOL. % CLASS 1	5.	5.	5.	5.	5.
6. VOL. % CLASS 2	6.	6.	6.	6.	6.
7. VOL. % CLASS 3	7.	7.	7.	7.	7.
8. THINNER RATE 1	8.	8.	8.	8.	8.
9. THINNER RATE 2	9.	9.	9.	9.	9.
10. THINNER RATE 3	10.	10.	10.	10.	10.
11. CONTROL EFFICIENCY	11.	11.	11.	11.	11.
12. #1 VOL. % CLASS 1	12.	12.	12.	12.	12.
13. #1 VOL. % CLASS 2	13.	13.	13.	13.	13.
14. #1 VOL. % CLASS 3	14.	14.	14.	14	14.
15. #2 VOL. % CLASS 1	15.	15.	15.	15.	15.
16. #2 VOL. % CLASS 2	16.	16.	16.	16.	16.
17. #2 VOL. % CLASS 3	17.	17.	17.	17.	17.
18. #3 VOL. % CLASS 1	18.	18.	18.	18.	18.
19. #3 VOL. % CLASS 2	19.	19.	19.	19.	19.
20. #3 VOL. % CLASS 3	20.	20.	20.	20.	20.
21. B	21.	21.	21.	21.	21.
22. GAL/YR CLASS 1	22.	22.	22.	22.	22.
23. GAL/YR CLASS 2	23.	23.	23.	23.	23.
24. GAL/YR CLASS 3	24.	24.	24.	24.	24.
25. C	25.	25.	25.	25.	25.

FORMULATION USED	POTENTIAL SOLVENT	SOLVENT CONTROLLED	SOLVENT EMITTED	PCR SOLV. BY DEF.	1,2,3 IN PCR MATERIAL	1,2,3 IN PCR MATERIAL	CLASS 1	CLASS 2	CLASS 3

PCR 1	NPCR 1	PCR 2	NPCR 2	PCR 3	NPCR 3

Exhibit 9

HYDROCARBON DATA SUMMARY

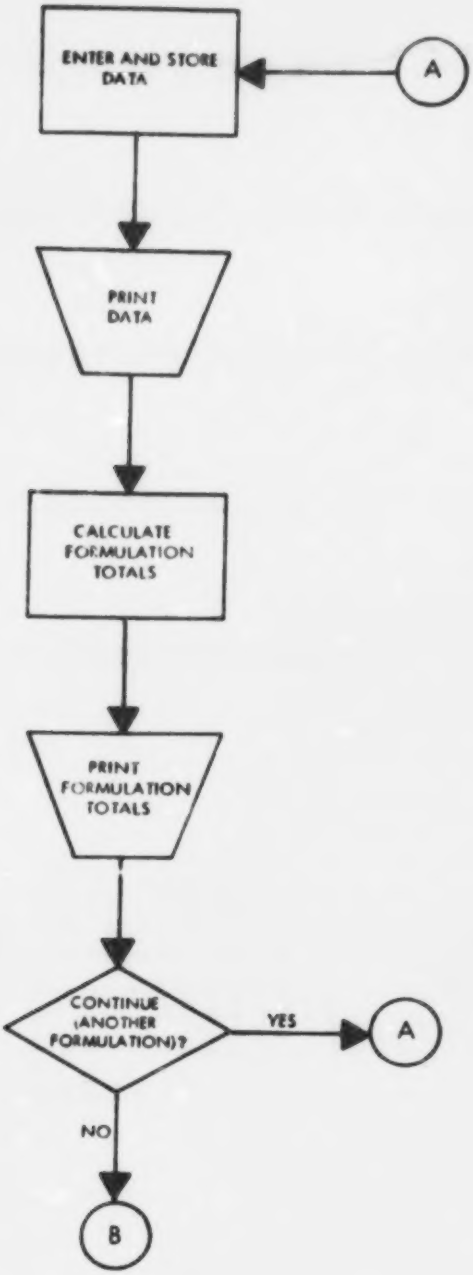
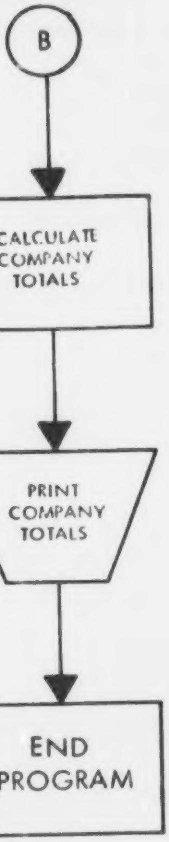

ENTER AND STORE DATA
A
PRINT DATA
CALCULATE FORMULATION TOTALS
PRINT FORMULATION TOTALS
CONTINUE (ANOTHER FORMULATION)?
YES
A
NO
B

Exhibit 9 (con.)

HYDROCARBON DATA SUMMARY


B
CALCULATE COMPANY TOTALS
PRINT COMPANY TOTALS
END PROGRAM

Chicago Department of Environmental Control

Exhibit 10

REQUIREMENTS FOR WATCH

1. ASA received for any area within state

OR

2. National Weather Service forecast for next 24 hours does not indicate substantial improvement.

AND

two hour average of following pollutants at any monitoring station have reached or exceeded these levels;

SO_2	.30	ppm for 2 hr. average
COH	5.0	COH's for 2 hr. average
Product of SO_2 x COH	1.0	for 2 hr. average
CO	30	ppm for 2 hr. average
O_3	.07	ppm for 2 hr. average
NO_2	.40	ppm for 2 hr. average

REQUIREMENTS FOR YELLOW ALERT

1. Watch in effect for four hours where yellow alert is to be declared

AND

2. Official National Weather Service forecast for next 12 hours does not indicate substantial improvement

AND

Exhibit 10 (con.)

3. Yellow alert levels at any monitoring station for the following pollutants reach or exceed these levels.

SO_2	.30	ppm for 4 hr. average
COH	3.0	COH's for 24 hr. average
Product of COH x SO_2	1.0	for 4 hr. average
Product of COH x SO_2	.20	for 24 hr. average
CO	15	ppm for 8 hr. average
O_3	.10	ppm for 1 hr. average
NO_2	.60	ppm for 1 hr. average
NO_2	.15	ppm for 24 hr. average

REQUIREMENTS FOR RED ALERT

1. Yellow alert in effect for 4 hours where red alert is to be declared

AND

2. Official National Weather Service forecast for next 12 hours does not indicate substantial improvement AND EITHER OF THE FOLLOWING CONDITIONS IS MET:

EITHER

Exhibit 10 (con.)

3a. Red alert levels at any monitoring station for the following pollutants reach or exceed these levels;

SO_2	.35 ppm for 4 hr. average
COH	5.0 COH's for 24 hr. average
Product of SO_2 x COH	2.0 for 4 hr. average
Product of SO_2 x COH	.80 for 24 hr. average
CO	30 ppm for 8 hr. average
O_3	.40 ppm for 1 hr. average
NO_2	1.20 ppm for 1 hr. average
NO_2	.30 ppm for 24 hr. average

OR

3b. Yellow alert levels at any monitoring station for the following pollutant reach or exceed these levels;

SO_2	.30 ppm for 24 hr. average
COH	3.0 COH's for 24 hr. average
Product of COH x SO_2	.20 for 24 hr. average
CO	15 ppm for 24 hr. average
O_3	.10 ppm for 24 hr. average
NO_2	.15 ppm for 24 hr. average

REQUIREMENTS FOR EMERGENCY

1. Red alert has been in effect for 12 hours where emergency is to be declared.

Exhibit 10 (con.)

2. Official National Weather Service forecast for next 12 hours does not indicate substantial improvement AND ANY OF THE FOLLOWING CONDITIONS IS MET:

EITHER

3a. Emergency levels at any monitoring station for the following pollutants reach or exceed these levels;

SO_2	.40 ppm for 4 hr. average
COH	7.0 COH's for 24 hr. average
Product of SO_2 x COH	2.40 for 4 hr. average
Product of SO_2 x COH	1.20 for 24 hr. average
CO	40 ppm for 8 hr. average
O_3	.60 ppm for 1 hr. average
NO_2	1.6 ppm for 1 hr. average
NO_2	.40 ppm for 24 hr. average

OR

3b. Red alert levels at any monitoring station for the following pollutants reach or exceed these levels;

SO_2	.35 ppm for 24 hr. average
COH	5.0 COH's for 24 hr. average
Product of SO_2 x COH	.80 for 24 hr. average
CO	30 ppm for 24 hr. average
O_3	.40 ppm for 24 hr. average
NO_2	.30 ppm for 24 hr. average

Exhibit 10 (con.)

OR

3c. Yellow alert levels at any monitoring station for the following pollutants reach or exceed these levels;

SO_2	.30 ppm for 36 hr. average
COH	3.0 COH's for 36 hr. average
Products of COH x SO_2	.20 for 36 hr. average
CO	15 ppm for 36 hr. average
O_3	.10 ppm for 36 hr. average
NO_2	.15 ppm for 36 hr. average

DISCUSSION

THE FLOOR: To what extent is Chicago a model for other cities?

MR. CZERNIAK: As of this point, we are not really dealing with other cities, and they have not contacted us about our program. Possibly with this paper there will be some interest. And we would be glad to help out anyone who would be interested.

DR. HERMAN F. KRAYBILL (National Cancer Institute, Bethesda, Maryland): You were speaking lately about the air emissions and earlier, I guess, about the water emissions. I take it that these reached Lake Michigan, Lake Huron; is that correct? Would they reach Lake Michigan?

MR. CZERNIAK: In this paper, I was not speaking about water emissions. But the effluent, as it is from these processes that we are considering today, would not reach Lake Michigan.

DR. KRAYBILL: Other bodies of water?

MR. CZERNIAK: Other bodies of water, such--

DR. KRAYBILL: Are those other sources for drinking water?

MR. CZERNIAK: They are used by some other cities farther downstream.

DR. KRAYBILL: Have you made any correlation into this and the levels in the drinking water?

MR. CZERNIAK: No, we have not, not under this project. Possibly that will be a further part of the study.

MR. CHARLES R. WARNER (National Cancer Institute, Bethesda, Maryland): Could I ask about some of the exempt solvents? What are the identities?

MR. CZERNIAK: There is quite a list, and many of them have tradenames. In other words, they do not give the chemical name of the chemical. The list is just interminable; if you give me your name, I could certainly get you a list of those.

DR. KRAYBILL: Another question, again, on the area. Who does the monitoring, the plant?

MR. CZERNIAK: When a test is required, we will be doing the testing.

THE FLOOR: Have you traced how far away from that particular plant the concentration of this effluent carries?

MR. CZERNIAK: No, not under this program. But from our technical services people, I understand that there is a project proposed by the Navy in which we would trace certain pollutants farther downstream.

THE FLOOR: How did you arrive at your guidelines for high solids or aqueous?

MR. CZERNIAK: These guidelines, I believe, are in Los Angeles Rule 66, and they are also in the Illinois EPA regulations. And to some extent, they were based on that. They differ only in the actual percentages allowed.

MR. DONALD M. GARDNER (Monsanto Corporation, Indian Orchard, Massachusetts): What percentages of companies got into compliance by switching to ultraviolet curing inks?

MR. CZERNIAK: The companies that are currently using ultraviolet inks are classified, probably, in the last 25 percent. They use the combination of methods. I will not give their names. They are some of the largest emitters. And they have just developed the technology in the coatings to be able to do this.

Just last week I was at one company that began production. It has been pretty successful, and they plan to use additional units in the future.

22 September 1975

Session II:

ENVIRONMENTAL IMPACT OF CHEMICALS USED

William D. Schaeffer, Ph.D.*
Chairman

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*Director, Research Department, Graphic Arts Technical Foundation, Pittsburgh, Pennsylvania

SESSION INTRODUCTION

William D. Schaeffer, Ph.D.
Session Chairman

I am delighted to be here and want to express my appreciation to Dr. Fisher, who organized the conference on behalf of the Environmental Protection Agency, and to Mr. Ayer and his associates of Research Triangle Institute for doing so much in the development of the background work that goes into organizing a conference of this type.

I am sure that many of you out there in the audience are not totally aware, even after this morning's sessions and excellent presentations, of the entire nature of the graphic arts industry. I thought that, for the first moment or so, I might describe a few of the elements in the industry, namely my own organization and its related activities.

The Graphic Arts Technical Foundation is a corporate membership foundation devoted to technology and education in the graphic arts industry. It currently has about 1,000 corporate members, 80 percent in North America and approximately 20 percent distributed among the rest of the world.

We've become aware of the environment. As a matter of fact, some of our first studies went back to 1967 and have gradually grown since. But the problems of the environment by no means start or stop with one association, as you will hear in the following two sessions. Because of the fragmentation of the industry, about which I will have more to say later and which you will hear a number of speakers address themselves to, it was felt that a broader, more inclusive effort had to be made within the industry in order to deal with the types of problems that we will be learning about. The best way we could handle this problem was to try to bring all the groups in the industry together: the business associations, the technical associations, and the corporations themselves.

To that end, there was a move made back in 1971 to form what is called the Environmental Conservation Board of the Graphic Communications Industries, Incorporated, a long moniker. That group is really acting as a communications body today. Many of the actions taken on behalf of the industry are emanating from the voluntary involvement of the business associations and some of the largest corporations in the industry. We're attempting to speak on behalf of approximately 6,000 companies in the industry, represented by the approximately 20 associations in the ECB, as we call the Environmental Conservation Board. So much for background.

Let's get to the next two sessions and their general context, the environmental impact of chemicals used. I think the purpose of these two sessions is at least twofold. Certainly, the first purpose is awareness. The conference can make some of us more aware and can extend to others of us new awareness of the problems we in the industry and our associates in the government face in working with the diverse problems in this area. Our responsibility in this conference is to indicate the current status of knowledge and of the developments that are emanated from the many groups and organizations in the industry and in the government which have been directly involved in studies.

Perhaps it would be useful to our associates in the government to reinforce simply a few of the comments that were made this morning on the nature of the graphic arts or printing industry in the United States.

Under the industrial census, as you were told, the printing industry is classified number one in terms of number of establishments--approximately 40,000-- and employs more than 1 million persons. It was indicated this morning that approximately 50 percent of these companies employ something less than 100 people. The statistics in this area are, I think, even more dramatic than that particular point. More than 90 percent of the 18,000 commercial printing establishments have fewer than 50 employees, with almost 80 percent having fewer than 20 employees. Those statistics in themselves give you some idea of the nature of the problems that we face in dealing with an industry that is widespread geographically, but which is admittedly concentrated in certain urban areas.

The industry has in the past been severely segmented by differences in the printing processes, which were generally outlined to you this morning. Fortunately, the differences among companies, or the differences due to the utilization of different printing processes, are gradually disappearing, insofar as many, many plants have or are developing multiprocess capabilities. Residual, however, from ages past is a fragmentation among the product groups:

for example, fragmentation in terms of products such as newspapers; magazines; periodicals; commercial, legal, and package printing; metal decorating; etc. We can readily count more than 20 different product groups in the industry.

And fortunately or unfortunately, but a fact of life is that we have more than 200 business associations serving the various groups within the industry. Now communication, I think you can see, becomes something of a major problem under these circumstances.

Let's go back to the title of these next two sessions, because I would like to consider for a moment the implications of the words and phrases extracted from the title: namely, Environmental Impact of Chemicals Used.

In addressing ourselves to environmental impact within this conference, we certainly have to recognize the several levels of the environment that are involved. I think we should have to include the manufacturer of the basic chemicals, the formulator of chemicals and products, the industrial users--that would be the printer and/or packager and the user of the printed page and/or package--and finally, the waste collectors, the salvagers, the recyclers, and the disposers. In short, environmental impact within the framework of this conference could include much of society because communication is the name of the game, and the printed page is still fundamental to the communication process.

The breadth of the conference troubles me because of the scope and the magnitude of the problems that we are asked to consider in this brief period of time. The fact that the legislation and the regulations controlling the several environmental areas are different; the fact that EPA, the conference organizer, bears only partial responsibility for the environments in which we work and live; the fact that legislation and regulations were developed in many cases with limited scientific and medical knowledge; the fact that we in the laboratory and in the industry use many materials without adequate knowledge: all these facts we have to subordinate within the framework of the conference. The most important aspect of environmental impact is the scope and magnitude of the problems.

There are a few individuals, a few companies, a few agencies that may be able to recognize and deal with the problems in all their complexities.

Frankly, most of us in the industry cannot. Resources are finite, and they must be marshaled for use in the priority-project areas. Resources of the industry are very limited. I do not like to see them dissipated in shifting priorities and projects, and goodness knows we have had plenty of that.

Thus, in the course of the conference, I certainly would like to see--and I hope some more of you will make your feelings felt--that we are able to make some assessment of where our priorities are and, possibly, where they should be.

The scope of the environmental impact problem has been recognized, certainly, in the planning of this conference. In the next two sessions we are going to have speakers from printing companies, supplier companies, including the printing ink, paper, industry association speakers, government agency contributors and medical research personnel. More important than the sponsors of the speakers, however, are the scientific and medical disciplines in which the speakers are schooled.

Environmental impact is not a problem for chemists alone, not a problem for a physicist alone, not a problem for medical doctors alone, not a problem for industrial hygienists alone. It is another example of the multidisciplinary problem that many of us in the printing industry, which represents multidisciplinary approaches, have recognized. I don't think there is any question that we need this approach to assess and deal with the problems of environmental impact. Communications have to be made between people in these various disciplines if any progress is to be made at all.

We have an unusual opportunity in the next few days to talk with one another and to learn what we are doing, how we are making out in our approaches, and how we look at the nature of the general environmental impact problems that we face.

The second part of the session, entitled the Chemicals Used, seems simple enough to the chemists among us, despite the large numbers of chemicals involved. I would suggest to you, however, that specific chemical identification is frequently difficult. Commercial chemical supplies, first of all, do contain numerous components, which frequently are not identified chemically. Second, chemical products synthesized by the printing supply industry may or, more frequently, may not be identified as to chemical structures. Often, it has not been thought necessary, or even economic to do so.

And last, the influence of the printing process itself on the chemical structure has to be considered. Whether we are dealing with films, plates, development, or drying of heat set inks, comparatively little has been published to indicate the specific composition of the chemicals entering the environment.

Another factor of significant importance in this area is that the large majority of printing supplies is based on proprietary compositions. A few words were said in this direction this morning. In many cases the formulations and compositions represent major investments of companies, not only in assuring the performance of the product in the field, but also in safeguarding their own in-plant environment as well as that of their customer. Not surprisingly, information on specific chemical identification is often not provided readily. In addition, chemical identification in supplies and products can present real technical problems which are complicated by the traditional structure of the industry based on proprietary supplies.

In summary, then, the next two sessions are going to be dealing with environmental problems in the printing industry at several levels. Perhaps--I certainly hope--a sense of priorities will emerge.

This conference will go a long way toward establishing communication channels, both within the industry and between the industry and the government agencies. I think many of our speakers are going to be dealing directly with this communication problem.

TOXICOLOGICAL EVALUATION OF CHEMICALS USED IN THE PRINTING AND PRINTING INKS INDUSTRIES

Kingsley Kay, Ph.D.*

During the recent boom years, the graphic arts industry has been among the most active in growth and technical development. There has been a trend from letterpress to lithography, with the introduction of photo-sensitive polymers for plates. Radiation-sensitive polymers have been developed for use in solventless inks in order to meet ecological and energy requirements. However, it must be noted that flexography and gravure, high-speed processes, still require the use of liquid inks containing high-volatility solvents, many of which have been demonstrated to be neurotoxic. Apart from the foregoing there has been growing interest in the extent of occurrence of potential carcinogens in occupational situations. This has directed attention toward carcinogenicity evaluation of the materials commonly used in the printing industry, including ink pigments, solvents and the new polymers.

Site visits have been made to 25 companies in the printing and printing ink formulation industries of New York and New Jersey, with the purpose of identifying potentially toxic chemicals in the work environments and assessing the toxicological possibilities for damage to the health of exposed workers. In this effort there have been extensive consultations with management, engineering specialists and chemists, as well as with pertinent national trade associations, concerned unions, the Division of Organic Coatings and Plastics Chemistry of the American Chemical Society, the National Cancer Institute, and the International Agency for Research on Cancer.

This report will consider, among several aspects, the carcinogenic potential of chemicals in printing. It is therefore important to establish that several chromophores or metabolic products thereof have been found cancer-associated.

1. Monoazo compounds, first exemplified by carcinogenic dimethylaminoazobenzene (butter yellow).

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*Associate Professor, Environmental Sciences Laboratory, The Mount Sinai School of Medicine, New York, N.Y. 10029.

Supported by National Institute of Environmental Health Sciences Grant ES 00928 and American Cancer Society Grant R-53.

2. Disazobenzidines, shown to reduce (hepatic azoreductase) to benzidines and to be present in urine of monkeys fed the chromophore.
3. Triarylmethanes-amino derivatives.
4. Xanthenes-amino derivatives.
5. 4,4'-diaminostilbenes, numerous triazenes and triazines.

One enzyme, azoreductase, which breaks azo groups, has been identified in microsomal liver tissue, but there is conflicting evidence as to whether the azoreductase level quantitatively correlates with carcinogenicity. Nevertheless, in the case of disazobenzidines, the benzidine and 3,3'-dichlorobenzidine fragments have been shown independently to be carcinogenic. Furthermore, it has been reported from Japan that female kimono painters using disazobenzidines have experienced high bladder cancer incidence.

There are important problems in estimating carcinogenesis. To begin with, exposure to a carcinogen must cover a substantial proportion of the life span to eventualize in carcinogenicity, except in the case of newborn animals, which can develop cancer soon after exposure to a carcinogen. As an example, vinyl chloride was tested for 6 months on rats in 1961 and was found carcinogenically inactive. However, when the experiment was repeated in 1970, cancers attributable to the vinyl chloride were demonstrated at around 12 months. Another related aspect of carcinogenicity testing on animal models is the effect of noncarcinogenic toxicity on life span. For instance, the insecticide dieldrin is neurotoxic and hepatotoxic. Early experiments to determine its carcinogenicity produced misleading results because, at the level of dosage used, the dosed rats died from the neurotoxic and hepatotoxic action long before carcinogenicity could develop.

Another aspect of carcinogenicity testing on animals is the significance of injection-site tumors when metastages to other organs does not occur. Many experts consider injection-site tumors without metastases to be of low significance. The neoplastic significance, if any, of so called benign tumors has also aroused controversy, since, in some instances, withdrawal of the provoking agent has been found to result in regression of the growth. On the other hand, if dosage is continued, benign tumors may become neoplastic

Various species and strains have a propensity for developing tumors without the administration of carcinogenic chemicals, possibly due to unknown water, air, and food carcinogens. As a result, the number and variety of tumors occurring in dosed animals can prove difficult to differentiate reliably from the number and variety of the spontaneous type, even with the use of sophisticated statistical methods. Furthermore, the target organs may differ from species to species for the same chemical carcinogens and so may the characteristic organ cancers of the spontaneous type. Finally, it is known that housing conditions, age, sex, nutrition, and viruses influence the occurrence of spontaneous tumors.

There are several problems in identifying occupationally occurring chemicals as etiological agents in human cancer. In the first place, it requires upwards of 20 years of exposure to easily metabolized chemicals for cancer to develop in man, or a similar elapsed time during which organ deposits, such as lung asbestos, provide tissue insult when further exposure may have ceased. Thus, the occupational origin of some cancers in persons who have changed occupations or retired may not be recognized. The occupational exposure may also involve a complex of chemicals as well as those associated with cigarette smoking.

A most fundamental problem in identifying etiological agents of human carcinogenesis is the difficulty of assembling large enough worker cohorts either retrospectively or prospectively to permit valid statistical comparison of cancer incidence between the occupational cohort and the general population. This is especially true for cancers of organs such as the lung, which occur in relatively high incidence among the general population. If the cancers are of rarely occurring type, their occurrence in a worker group even in small incidence will be striking. This was dramatically demonstrated by the recent identification of vinyl chloride as etiological agent in the causation of hemangiosarcomas of the liver in polyvinyl chloride production workers. It was estimated that in all history only around 120 cases had been reported, whereas among a few hundred workers in one PVC plant, 4 cases of this hepatoma were recognized in a short period of time. For several reasons just set forth, evidence of carcinogenicity in laboratory models has sometimes been accepted under the Federal Occupational Safety and Health Act and the Food and Drugs Act in the absence of incontrovertible proof that a chemical carcinogen affects man.

INK PIGMENTS AND DYES

Many pigments and dyes were found in the formulation laboratories of the various printing ink concerns visited because they were "custom" businesses. However, only a limited number of color compounds were used in substantial quantities. In this situation, the president of a major New York printing ink concern cooperated by analyzing the extent of use of color components in the manufacture of his printing inks. A list of the 37 used in largest quantity was provided. These are shown in tables 1a-1c along with the data required for carcinogenic evaluation of the chemicals. The list was reviewed by the National Association of Printing Ink Manufacturers and was considered to be representative.

As shown in table 2, there were 4 components cancer-positive in man or animals, 15 probable by virtue of chemical class, and 5 were negative. The evidence was conflicting for four, and on nine no information could be found. Obviously pigments and dyes used in printing have not been comprehensively evaluated for carcinogenicity.

Recent findings on laboratory animals introduce the possibility of non-malignant kidney damage in persons exposed not only to lead pigments (refs. 44-47) but also to benzidine-based colorants (refs. 48-51) and 2-aminoanthraquinone (ref. 52).

In the printing ink establishments visited, the main occupational categories and potential colorant exposures were as shown in table 3. A controlling factor in colorant exposure is the necessity for a high degree of cleanliness to preserve the integrity of formulations during processing. Additionally, many colorants are worked up as pastes, though some are dry in the early stages of formulation and are dusty to handle.

The significance of the foregoing in relation to cancer risk must be deemed speculative pending the measurement of cancer incidence among the workers in printing ink formulation and printing.*

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*A recent personal communication from Dr. W. Fokkens, Rotterdamsch Radio-Therapeutisch Instituut, notes that higher than expected incidence of bladder cancer has been found in graphics industry workers.

Table 1a. A summary of findings on the carcinogenicity of 37 major printing ink constituents

Name of component	Generic name[1]	CI number[1]	Chemical class	Usage as % TiO_2	Species	Route of entry to the body	Exposure or dose level	Duration	Target organs	Lit. refs.
Titanium dioxide	CI pigment white 6	77891	Inorganic	100	–	–	–	–	–	No refs.
Lead chromate	No name	77600	$PbCrO_4$	40	Man and rats	Inhalation subcutan.	Occupatnl. 10% aqun.	Years 37 weeks	Lungs inj. site	1,2,3
Molybdate orange	CI pigment red 104	77605	$PbCrO_4$-$PbMoO_4$	20	See above	See above	See above	See above	See above	1,2,3
Phthalocyanine blue	CI pigment blue 15	74160	Copper complex	20	Mice	Subcutaneous	0.5 mg/wk	8 months	Nil	4
Calcium carbonate	No name	No number	$CaCo_3$	20	–	–	–	–	–	No refs.
Diarylide	CI pigment yellow 12	21090	Disazo benzidine[2]	15	Some disazobenzidines reduce (hepatic azoreductase) to carcinogenic 3,3'-dichlorobenzidine.					5-10, 11 (p. 241)
Alkali blue	CI acid blue 110	42750	Triphenyl methane deriv.	15	A variety of members of this chemical class have been found to be carcinogenic.					11 (p. 22), 12-17
Clay	No name	No number	Silicates	15	–	–	–	–	–	No refs.
Barium sulfate	CI pigment white 21-22	77120	$BaSO_4$	15	–	–	–	–	–	No refs.
Lithol red	CI pigment red 49	15630	Monoazo Na salt	10	Rats	Ingestion	0-1% of diet	2 years	Nil	18
Iron blue	CI pigment blue 27	77510	Ferric ferrocyanide	10	–	–	–	–	–	No refs.
Carbon	No name	No number	Elemental	10	Mice	Skin surf. subcutan.	Various	To 20 mo.	Skin injec. site	19-22

[1] Assigned by British Society of Dyers and Colourists, and the American Association of Textile Dyers and Colorists. Published as The Color Index.

[2] 3,3'-dichlorobenzidine ⇉ acetoacetanilide.

Table 1b. A summary of the findings on the carcinogenicity of 37 major printing ink constituents

Name of component	Generic name[1]	CI number[1]	Chemical class	Usage as % TiO_2	Species	Route of entry to the body	Exposure or dose level	Duration	Target organs	Lit. refs.
Magnesium carbonate	CI pigment white 18	77713	Inorganic	10	–	–	–	–	–	No refs.
Red lake C	CI pigment red 53	15585	Monoazo Na salt	7	Rats	Ingestion	0-1% diet Ba salt	2 years	Nil	27
Lithol rubine	CI pigment red 57	15850	Monoazo Na salt	7	Related members of this chemical class found carcinogenic.					11 (p. 200)
BON red	CI pigment red 52	15860	Monoazo Na salt	7	Related members of this chemical class found carcinogenic.					11 (p. 200)
Red 2B	CI pigment red 48	15865	Monoazo Na salt	5	Related members of this chemical class found carcinogenic.					11 (p. 200)
Rhodamine[2]	CI basic red 1	45160	Xanthene derivative	5	Conflicting experimental evidence.					11 (p. 23),24
Methyl violet	CI basic violet 1	42535	Triaryl methane	5	Conflicting experimental evidence.					11 (p. 22), 12-17,25
Victoria blue	CI basic blue 7	42595	Triaryl methane	5	A variety of members of this chemical class have been found to be carcinogenic.					11 (p. 22), 12-17
Phthalocyanine green	CI pigment green 7	74260	Chlorinated Cu complex	5	–	–	–	–	–	No refs.
Aluminum hydrate	CI pigment white 24	77002	Al_2O_3 and $Al_2(SO_4)_3(OH)_3$	5	Various experimental protocols.				Nil	26-31
Phloxine red	CI acid red 87	45380	Xanthene derivative	3	Conflicting experimental evidence.					11 (p. 23)
Naphthol red	CI pigment red 22	12315	Monoazo	2	Related members of this chemical class found carcinogenic.					11 (p. 200)

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[1] Assigned by British Society of Dyers and Colourists, and the American Association of Textile Dyers and Colorists. Published as The Color Index.

[2] Constitution number covers rhodamine 6G in The Color Index.

Table 1c. A summary of the findings on the carcinogenicity of 37 major printing ink constituents

Name of component	Generic name[1]	CI number[1]	Chemical class	Usage as % TiO_2	Species	Route of entry to the body	Exposure or dose level	Duration	Target organs	Lit. Refs.
Magenta[2]	CI basic violet 10	45170	Xanthene derivative	2	Conflicting experimental evidence.					11 (p. 23), 16,17,24, 32-36
Hansa yellow	CI pigment yellow 1	11680	Monoazo	2	Related members of this chemical class found carcinogenic.					11 (p. 200)
Bronze powder	CI pigment metal 2	77400	Copper-zinc-iron alloy	2	–	–	–	–	–	No refs.
Aluminum powder	No name	No number	Elemental	2	Various experimental protocols.				Nil	28,30, 37-39
Silica aerogel	No name	No number	SiO_2 amorphous	2	–	–	–	–	–	No refs.
Cadmium red	CI pigment red 108	77196	Cadmium selenide	<1	Other cadmium salts have been found carcinogenic to animals.					3,40,41
Fire red	CI pigment red 4	12085	Monoazo	<1	Related members of this chemical class found carcinogenic.					11 (p. 200)
Para red	CI pigment red 1	12070	Monoazo	<1	Related members of this chemical class found carcinogenic.					11 (p. 200)
Toluidine red	CI pigment red 3	12120	Monoazo	<1	Related members of this chemical class found carcinogenic.					11 (p. 200)
Diarylide orange	CI pigment orange 13	21110	Disazo benzidine[3]	<1	Some disazobenzidines reduce (hepatic azoreductase) to carcinogenic 3,3'-dichlorobenzidine.					5-10 and 11 (p. 241)
Dinitroaniline orange	CI pigment orange 5	12075	Monoazo	<1	Related members of this chemical class found carcinogenic.					11 (p. 200)
Cadmium yellow	CI pigment yellow 37	77199	Cadmium sulfide	<1	Rats	Subcutan. intramusc.	25 mg single 50 mg single	Up to 15 months	Injection site	40-41
Talc	–	–	Silicate	<1	Man	Inhalation	Various	Years	Lungs	42-43

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[1] Assigned by British Society of Dyers and Colourists, and the American Association of Textile Dyers and Colorists. Published in The Color Index.

[2] The constitution number covers rhodamine B in The Color Index, where magenta is either CI basic violet 14 (42510) or the phosphotungstomolybdic acid salt of rhodamine B (45170:2) listed as magenta lake B. CI basic violet 14 is a triphenylmethane triamino derivative.

[3] 3,3'-dichlorobenzidine ⇄ 3-methyl-1-phenyl-5-pyrazolone

Table 2. Condensed assessment of the carcinogenicity[1] of 37 printing ink color-related components including usage as percentage of TiO_2 used

Positive	% TiO_2	Probable[2]	% TiO_2	Conflicting evidence	% TiO_2	Negative[3]	% TiO_2	No Information[4]	% TiO_2
Lead chromate	40	2 disazo benzidines	15 <1	3 xanthenes	10	Phthalocyanine blue	20	Titanium dioxide	
Lead chromate-lead molybdate	20	2 triaryl methanes	20	1 triaryl methane	5	2 monoazos	17	Calcium carbonate	20
Carbon	10	9 monoazos	25			Aluminum hydrate	5	Clay	15
Cadmium sulfide	<1	Cadmium selenide	<1			Aluminum powder	2	Barium sulfate	15
		Talc	<1					Ferric ferrocyanide	10
								Magnesium carbonate	10
								Chlorinated copper complex	5
								Bronze powder	2
								Silica aerogel	2
Total 4	70+	Total 15	60+	Total 4	15	Total 5	44	Total 9	79

[1] in man and/or laboratory animals.

[2] A variety of members of these chemical classes have been found carcinogenic.

[3] Negative to the extent tested (see tables 1a to 1c for details).

[4] No information on these or related members of their chemical classes.

Table 3. Typical occupations in printing ink formulation

Occupation	Estimated pigment exposure
Bander and labeler	Slight
Combination man	Slight
Container washer	Medium
Driver	Slight
Shipper and receiver	Slight
Maintenance	Medium
Messenger	Slight
Millhand	Medium
Porter	Medium
Rollermaker	Slight
Sewing machine operator	Slight
Utility man	Medium
Varnishman	Slight
Weigher and mixer	Substantial
Working foreman	Medium
Laboratory staff	Substantial

SOLVENTS

High-volatility solvents are used in formulation of liquid inks for flexography and gravure, where fast drying is required. In the printing establishments visited, the chlorinated hydrocarbon solvents--methyl chloroform and methylene chloride--were employed for hand cleaning of typeface. It was an operation with substantial albeit intermittent exposure for the typeface cleaner and adjacent workers.

An extensive range of volatile solvents was seen on the site visits. Details on others were provided by the National Association of Printing Ink Manufacturers. Table 4 lists the solvents, concentrations used, and the threshold limit values recommended by the American Conference of Governmental Industrial Hygienists. Table 5 summarizes toxicological data on selected solvents, including some used in printing and ink formulation.

It is now known that methylene chloride is metabolized in man to carbon monoxide (refs. 111-117). Stewart et al. (ref. 111) found abnormal levels of

Table 4. Solvents used in gravure, flexography, and screen printing inks

	Percentage in organic pigment ink	Percentage in inorganic pigment ink	TLV[1]
Acetate ester of C_2-C_4	12	10	400
Aromatic hydrocarbon[2]	6	6	-
Bis-(2-ethoxy, ethoxy)ethanol	2-4	2-4	-
Diethylaminoethanol	3-5	3-4	-
Ethanol (denatured)	0-45	5-29	1000
Ethyleneglycolmonoethylether	3	0	-
n-Heptane (•>10% aromatic)	3-14	3-7	400
n-Hexane	as above	as above	100
Isopropanol	2-14	0-12	400
Isopropyl acetate	10-20	6-15	250
Lactol spirits[3]	4-51	12-30	-
Methanol	12	5	200
Methyl ethyl ketone	0	11	200
Mineral spirits[4]	58	53	-
n-Propanol	0-14	5-18	200
Textile spirits[5]	43	30	-
Toluene	5-62	3-7	100

[1] ppm in 1974.

[2] Aromatic hydrocarbon solvent-C_8 and higher aromatic hydrocarbons, 97%; saturated hydrocarbons, 3%; b.p. range 370°-410° F.

[3] Lactol spirits – C_6-C_8 paraffins, 48%; C_6 to C_8 cycloparaffins, 35%; other than C_8-C_9, 10%; b.p. range 260°-300° F.

[4] Mineral spirits – saturated aliphatic hydrocarbons, 82.6%; aromatic (toluol or ethyl benzene), 15%; C_8 and higher hydrocarbons, 2.4%; b.p. circa 313 ° F.

[5] Textile spirits – C_5-C_6 paraffins, 70%; C_5-C_6 cycloparaffins, 24%; aromatics, 6%; b.p. circa 150° F.

Table 5. Target organs in the systemic toxicity[1] of selected industrial solvents[2]

Solvent	Carcinogenic	Neurotoxic	Nephrotoxic	Hepatotoxic and other
Benzene	Leukemongenic –man 53-59 Neg. –rats 59a	Narcotic[3] 60, 61	No info.[6]	Bone marrow 63,64 Cardiac senst. 65
Carbon tetra-chloride	Liver 66-70	PN[4], hypotensive 71-74	TD[5]	Nonmalignant 75,76 Cardiac senst. 65
Chloroform	Liver 77	Anesthetic, hypotensive 78-80	TD 78-80	Nonmalignant 81 Cardiac senst. 65
Dimethyl-nitrosamine	Liver, kidney, etc., 82-89	No info.	Glomerular 90	Nonmalignant 91
Diethylene glycol	Bladder 92 No info.	Narcotic, CNS depressant 93-95	TD 92,96	Nonmalignant 92,96
Ethylene dibromide	Stomach 97, 97a	CNS depressant 98 (p. 1285)	Tubular swelling 99	Fatty infiltration 99
n-Hexane	No info.	PN 100	No info.	No info.
Methyl-chloroform	No info.	CNS depressant, hypotensive, 101,102	No info.	Mild 101,103-105 Cardiac senst. 106-109
Methylene chloride	No info.	CNS depressant 98 (p. 1259) 110	No info.	No info.; converts to CO, 111-117
Methyl n-butyl ketone	No info.	PN (motor) 118-125	Tubular congestion 98 (p. 1737)	Congestion 98 (p. 1737)
Toluene	No info.	Narcotic 98 (p. 1226), 126	TD, anuria 126,127	Jaundice 127
Trichlor-ethylene	Liver (tentative) 128,129	PN; cranial 130-133	TD; acute renal failure, 79,134	Slightly 135 Cardiac senst. 65
Turpentine	No info.	CNS effects 78	Hematuria, albuminuria 136	No info.

[1] In man and/or laboratory animals.

[2] Numbers in the table refer to the bibliography. References are selected when a substantial literature exists.

[3] In large doses.

[4] Peripheral neuropathy.

[5] Tubular damage.

[6] The reader is cautioned that the front page abstract of German reference 62 has "benzin" erroneously translated as "benzene." The correct translation is "benzine." There is no published evidence at hand identifying benzene as nephrotoxic.

carboxyhemoglobin in blood (6 to 8 percent) after human exposure at levels below the then-prevailing TLV (500 ppm). Signs of central nervous system depression were also demonstrated, using the visual evoked response test, which provided a measure of the cerebral electric response to a pulse of light (refs. 137-138).

It has been known for several years that cytochrome P450 is inhibited by carbon monoxide in vitro and in the housefly. The literature was reviewed in 1969 (ref. 139). This effect was demonstrated in vivo with rats (ref. 140) in an experiment which showed that hexobarbital and zoxazolamine metabolism were reduced in rats exposed to carbon monoxide (at substantial dosages). Since methylene chloride has been found to produce carbon monoxide as a metabolic product, reduction in drug metabolic activity of exposed workers might be interesting to test for. This is especially noteworthy in that a reduction in drug metabolism may change the reponse to a number of drugs, such as warfarin and perhaps more importantly, alcohol, and undoubtedly the carcinogenic polycyclic hydrocarbons, whose metabolism in the body responds to the variations in the activity of the mixed-function oxidizing enzymes.

There is now evidence (ref. 141) that 1,1,1-trichlorethane stimulates the drug-metabolizing power of the liver, which can lead to increased drug metabolism. This effect may be reflected in levels of body burdens of DDT and other adipose-stored chlorinated hydrocarbons. Most volatile solvents are soluble in fat and fat-solubilizing. It may therefore be supposed that they are stored in body fat. That there are body burdens of solvents in exposed persons has been established by breath analysis (ref. 142).

Table 5 shows that many solvents produce prenarcotic effects as well as abnormalities of nerve and muscle in over-exposed persons. EEG and memory tests have been found useful as indicators of disturbances in the central nervous system following exposure to a number of chlorinated hydrocarbons, for instance the tests in 1960 by Chalupa et al. (ref. 143). Persons exposed to 350 and 450 ppm of 1,1,1-trichlorethane (TLV 350 ppm) have been tested for psychophysiological function by means of: 1) a perception test with tachistoscopic presentation, 2) the Weschsler Memory Scale, 3) a complex reaction time test, and 4) a manual dexterity test. There was little evidence of psychophysiological change (ref. 144). Furthermore, the extent of statistical work involved does not encourage this approach. It should be noted, however, that 110 ppm of trichlorethylene (TLV 100 ppm) caused a very significant decrease in performance ability by all tests (ref. 145). Other test batteries have been developed for trichlorethylene (ref. 146) and methylene chloride (ref. 147).

In 1970, neuromuscular function of workers exposed to chlorinated hydrocarbon insecticides was examined (ref. 148). EMG signs of impaired nerve and muscle function were found in 4 percent of the exposed. So far no reports of use of EMG on workers exposed to chlorinated hydrocarbon solvents have been found. It is pertinent to note that the absorption of the volatile solvents would be at a much higher level than for the chlorinated hydrocarbon insecticides and presumably would affect the EMG of a higher percentage of subjects.

No environmental data on the level of exposure of proof pullers and type cleaners to the cleaning solvents have been found in the literature. Such measurements should be carried out as a basis for interpreting the findings from clinical examinations.

Methylchloroform has been shown to sensitize hearts of experimental animals to stress-induced chemicals of the adrenalin class (table 5), but similar effects on workers have not been reported.

Chloroform, carbon tetrachloride, and tentatively trichlorethylene have been incriminated as cancer-producing in laboratory animals (see table 5). Methylchloroform is currently under test (ref. 149). A substantial number of chlorinated hydrocarbon pesticides has been shown to be carcinogenic in laboratory tests over recent years (ref. 150). Apart from chlorinated hydrocarbon solvents, exposure to benzene has been shown to be associated with leukemia in workers (see table 5). This may be of great health significance since it has long been known that toluene and other hydrocarbon solvents can contain benzene as a process impurity. Not withstanding, benzene has not yet been shown to be carcinogenic in animal models (59a).

CANCER AMONG PRINTERS

It was found that ink was heavily dispersed into the workroom atmosphere during newspaper printing, to such an extent that a clean piece of paper placed on printing equipment was very soon blackened by atmospheric fallout. Clearly, printing ink was entering the lungs of exposed personnel. Nevertheless, occurrence of lung neoplasias or pulmonary defects in newspaper printers, in excess of the incidence in the average population, has not yet been established. As indicated by footnote at the end of the Ink Pigments and Dyes section, excessive bladder cancer has been noted in the graphics industry in the Netherlands.

In 1955, Ask-Upmark (ref. 151) found the bronchogenic cancer incidence of a group of typographers to be 18 times higher than normal (without adjustment for smoking habits). Dunn and Weir (ref. 152) followed the cancer experience of several occupations progressively and concluded in 1965 that printers did not show higher than normal incidence. A small excess of lung cancer deaths in British newpaper workers was noted by Moss et al. (ref. 153) for the period 1952-1966.

Several years ago, 22 printing inks of unidentified composition were tested in England by subcutaneous injection in mice (ref. 154). Seventeen were negative and five caused injection site neoplasms, of which two showed metastases to the lung. Indeed, as long ago as 1929, Steinbruck (refs. 155-156) painted mouse skin with a printing ink and produced skin epitheliomas with lung metastases, and lymphomas.

Much investigation of the carcinogenicity of carbon has been carried out (refs. 19-22) and it would appear that apart from source differences, biological activity is dependent on particle size and adsorptivity (ref. 22). Carbon blacks of average particle diameter 17 mμ tenaciously held benzo[a]-pyrene and were biologically inactive. However the presence of the eluent tricaprylin evoked carcinogenicity at sites of subcutaneous injection. It would have to be determined whether the high-boiling oils used with carbon black in inks would also act as eluents for cancer-producing chemicals adsorbed on the carbon.

LEAD

Apart from consideration of lead chromate as a pigment, it may be mentioned that in 1943, Black (ref. 157) advanced lead as a possible inciting factor in bronchogenic carcinoma. In 1963, Dingwall-Fordyce and Lane (ref. 158) reported no association between lead exposure and incidence of malignant neoplasms in a small cohort of battery workers. More recently, lead phosphate, acetate, and tetraethyl lead have been found to produce cancers in laboratory animals (ref. 159).

The problem of a lead hazard in the printing industry was widely investigated many years ago (refs. 160-173). Measures to control exposure to lead vapor and dust were introduced throughout the industry, with the result that classical lead poisoning cases are rare today. However, with more refined techniques available for estimating functional abnormalities of nerve and muscle, reexamination of this aspect would be desirable.

It is now believed that lead acts as a competitive inhibitor of the mechanism for release of acetylcholine at synaptic and neuroeffector junctions. Normally calcium fulfills this role. Peripheral neuropathy has been encountered in overexposed lead workers (and pica-eating children). For instance, Catton et al. (ref. 174) found a minimal defect of peripheral nerve function in a group of lead battery workers without clinical evidence of a neurological lesion. Abnormal chronaxie was described among Japanese printers in 1936 (ref. 175). Behavioral aspects of lead exposure were dealt with last year (refs. 176,177).

Thus, examination for functional abnormalities of nerve and muscle in printers might be considered if, for instance, blood levels proved to be in the region 40 μg lead per 100 ml blood and over. In view of the demonstrated effects of lead on the CNS and on peripheral nerve and muscle function (ref. 178), it is suggested that an assessment of the accident frequency of typographers would be rational. In 1963 it was reported (ref. 158) that cerebrovascular deaths were of higher-than-normal incidence in a small population of battery workers. However, other investigators (ref. 179) failed to find a relationship between lead exposure and hypertension.

AMMONIA EXPOSURE

The use of large tanks of anhydrous ammonia adjunct to photo-offset machines was found to be associated with gassings from time to time due to faulty lines from tanks. There is also a continuous ammonia exposure during normal operation of the machines. The amount of ammonia released varies from machine to machine and no doubt depends on servicing. There should be environmental assessment of the levels of ammonia present in the air adjacent to the machines.

Two papers from Scandinavia describe cerebral effects of acute ammonia intoxication (refs. 180,181). Intraperitoneally injected ammonia has been found to be rapidly taken up by red cells, with a subsequent flight of K^+, but no change in Na^+ (ref. 182).

Some consideration should be given to pulmonary response of exposed workers since it is known that ammonia, at least in high air concentrations, induces a pneumonitic response.

POLYMERS

Evaluation of the potential toxicity of polymers used in the printing trade has been initiated on the basis of observations made during the site visits to 25 establishments. Many well-known polymers are used in printing inks to bind pigment to the printed surface. Conventional plasticizers and oxidation accelerators are also ink ingredients. The recent development of solventless inks has resulted in the introduction of an extensive range of new polymers having radiation-sensitive properties for use in photolithography inks and plate coatings. A toxicity evaluation of polymers used in printing will be presented at a later date.

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DISCUSSION

MR. THEOPHILUS R. CARSON (Food and Drug Administration, Washington, D.C.): On this carbon, is it possible that it could be contaminated with PNA, polyneuclear aromatics? As a food additive, we even check solvents for PNA's, because this is where the greatest amount of impurities could be found.

DR. KAY: Yes. I should have mentioned that. That is what I was talking about; carcinogens in carbon black are believed to be polycyclic aromatic hydrocarbons.

GENERAL CHAIRMAN FISHER: In this regard, I would just like to interject what happened at the first conference in this series, which was on the rubber industry, where we discussed the question of whether or not carbon black was a carcinogen. We had three speakers on the subject, and a rather heated discussion which went well into the evening.

There definitely are different points of view. My overall impression is that there appears to be no question but that carbon black does have adsorbed on it materials which in other contexts are known carcinogens--polynuclear aromatics. There also appears to be fairly strong evidence, at least under injection or inhalation-type conditions, that these materials are not removed from the carbon black and do not seem to have the effects that they would have if administered alone, without the carbon black.

Now as to whether or not in the presence of an organic solvent during administration, these may come off is a question which I don't think anybody really is able to answer at this point.

DR. KAY: It has been said by Steiner that the reason it has not been possible to produce lung cancers in laboratory animals with carbon alone is because the lung does not contain any waxes like the skin. And Steiner claims that you can produce cancers with carbon black on skin because you have the wax in the skin, and the wax acts as an eluent. I think as long as some carbon blacks have been shown to be carcinogenic in animals, we have to take that point of view about all of them.

CHAIRMAN SCHAEFFER: May the Chairman ask a question of that point? Are we sure that we are talking about some carbon blacks or are we talking about ground charcoal? Ground charcoal, I think, definitely has been cited. I am not sure about some carbon ...

DR. KAY: I am including ground charcoal.

CHAIRMAN SCHAEFFER: Okay.

DR. KAY: I guess carbon black is ...

CHAIRMAN SCHAEFFER: Is not ground charcoal.

DR. KAY: ... not the best description.

CHAIRMAN SCHAEFFER: No.

DR. KAY: I think this does apply to ground charcoal. In fact I know that it has been studied.

CHAIRMAN SCHAEFFER: I think there is one more question here, please.

MR. GEORGE A. REMUS (R. R. Donnelley Company, Chicago, Illinois): Has polyvinyl chloride been shown to be carcinogenic?

DR. KAY: Not to my knowledge.

POTENTIAL HAZARDS OF ORGANIC SOLVENTS IN THE GRAPHIC ARTS INDUSTRY

Jacqueline M. Fetsko*

Abstract

Physical, chemical, and other data relevant to fire and health hazards were compiled for 123 organic solvents. The selection of solvents was based on use by the printing ink industry as ingredients in inks, intermediates, or washup solvents.

Analysis of the data indicates that the typical organic solvent is apt to be flammable, to cause irritation of some form, and, if absorbed into the body, to depress the central nervous system or be injurious to a vital organ, or both.

The potential hazards may be minimized by adequate ventilation to avoid flammable- or toxic-vapor concentrations and by strict hygienic measures to prevent skin contact.

By now, all of you should be aware, either from your own experience or from attendance at this conference, that organic solvents are very important chemicals in the graphic arts industry. You have heard Mr. Carpenter (ref. 1) state that 700 million pounds of organic solvents are used in printing inks each year. This quantity probably does not include the hundreds of pounds of press-side diluents and washup solvents that are also used.

One does not have to go to the graphic arts industry to be involved with organic solvents. Indeed, organic solvents play a very important role throughout modern society and technology: gasoline, antifreezes, and brake and transmission fluids to run our autos, trucks and buses; dry cleaning fluids; after-share lotions and other cosmetics; adhesives, paints, and paint thinners; and agricultural pesticides.

For many years industrial hygienists and safety engineers have viewed this growing increase in the use of organic solvents with alarm, because if used without proper control, the vast majority of them are to some extent hazardous. These hazards are now being recognized by many Government agencies such as EPA, which is sponsoring this conference, OSHA, and others who are promulgating regulations to protect the working man, the consumer, and our environment.

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*Assistant Research Director, National Printing Ink Research Institute, Sinclair Laboratory, Lehigh University, Bethlehem, Pennsylvania.

As a natural consequence, organic solvents were given first priority when the National Association of Printing Ink Manufacturers commissioned the Printing Ink Institute at Lehigh to start compiling data on the hazardous properties of raw materials. The purpose of these compilations is to make the users of the raw materials, whether it is the inkmaker himself or his customer or supplier, aware of what the hazards are so that they can take proper preventive measures.

Volume 1 of the Raw Materials Data Handbook, which was published approximately a year and a half ago (ref. 2), covers 123 nonproprietary solvents. There are hundreds more proprietary solvents, but these will be the subject of a subsequent compilation.

The compilation of the 123 organic solvents covers physical and chemical properties, fire-hazard data, health-hazard data, and other data of interest to the formulator. The Handbook Data Sheet includes a clear, concise summary of hazards so that, rather than read through the entire sheet, one can get an immediate idea of the important hazards for any given solvent. A separate Data Supplement contains information applicable to organic solvents in general. The Supplement, in combination with the individual Data Sheets, provides all information required for filling out a "raw materials data sheet."

For added convenience, numerical data from the Data Sheet were tabulated into Summary Tables by chemical family. Of the entire volume, the Summary Tables are probably the most used. They permit one to examine how certain properties change with molecular weight. Special codes also indicate the solvents that are photochemically reactive, serious irritants, and cumulative poisons.

Perusal of the contents of the Handbook readily suggests that the typical organic solvent possesses the following potential hazards:

1. Flammability,
2. Irritation:
    a. skin contact
    b. eye contact
    c. exposure to vapors,

3. Depression of the central nervous system, and/or
4. Organic injury from cumulative absorption:
    a. exposure to vapors
    b. skin absorption.

In the following summary, it will become apparent that the hazards cited are capabilities. Given adequate controls and preventive measures, no solvent need be a source of damage to life or property. It will also become apparent that the two most important controls are adequate ventillation and prevention of skin contact.

Flammability

As seen in table 1, only 3 of the 123 solvents covered in the Handbook are totally nonflammable and nonburnable. All others will sustain combustion under the "right" set of conditions. At least one-third are Class I flammables, that is, they have flash points below 100° F (37.7° C). This category includes all four nitroalkanes, most of the hydrocarbons, and, except for the glycol derivatives, about 50 percent of the oxygenated solvents.

Added dangers are explosion, which frequently accompanies fires involving highly volatile solvents under confinement, and the toxic nature of fumes given off as combustion products. The latter is especially true in the case of chlorinated and nitrogen-containing compounds.

Fire should be by all means avoidable in any industrial operation. First of all, in order for a fire to occur, there must be three essential elements:

1. a minimum temperature,
2. proper ratio of oxygen to vapor, and
3. a source of ignition.

Remove any one, preferably two, and the prospects of fire will be essentially nil. For example, adequate ventilation can do much to eliminate number two--the proper ratio of oxygen to vapor.

One of the reasons that physical properties must be compiled in addition to fire-hazard properties becomes very apparent when considering fire extinguishing methods. According to the National Fire Prevention Association (ref. 3), water is an effective extinguishing media only if the material:

Table 1. Flammability of organic solvents

Chemical family	Total #	Flammable (flash point under 100° F)	Combustible (flash point over 100° F)	Non-burnable at 1500° F
Hydrocarbons				
Aliphatic	3	3	-	-
Aromatic	4	4	-	-
Distillates	5	2	3	-
Oxygenated				
Alcohols	17	7	10	-
Esters (of alcohols)	13	7	6	-
Ketones	15	6	9	-
Ethers and oxides	7	5	1	1[a]
Glycol derivatives				
Glycols	9	-	9	-
Glycol ethers	24	1	23	-
Glycol esters	6	-	6	-
Other				
Chlorinated hydrocarbons	6	1	3[b]	2
Nitroalkanes	4	4[c]	-	-
NH compounds	10	-	10	-
Total	123	40	120	3

[a] Water.

[b] No flash point but autoignition temperature below 1500° F.

[c] May explode when confined liquid is shocked.

1. has a flash point above 100° F,
2. is insoluble in water,
3. has a specific gravity greater than water.

Condition number one--flash point above 100° F--automatically means that water is not an effective extinguishing agent for all Class I flammables. Few of the remaining solvents comply with the other two physical properties. Furthermore, if the solvent has a flash point above 212° F, water can cause spattering. Consequently, rather than water, carbon dioxide or dry chemicals are recommended for small fires and foam for large fires.

Irritation

Dermatitis. Because of the widespread prevalence of skin contact with solvents, dermatitis is the most frequent cause for complaint in the graphic arts industry (ref. 4). It should be pointed out, however, that a solvent is defined as a substance which dissolves another substance. One of the substances which organic solvents dissolve is fat or oil. So it is obvious that the very material used to clean ink off a press will also invariably remove the natural fats and oils in the human skin. The potential of this and other types of dermatitis is summarized as follows:

1. Fat and oil solvents. Aromatic and chlorinated hydrocarbons are excellent degreasers and may therefore be expected to cause a defatting-type of dermatitis after relatively few exposures.
2. Protein solvents. Since body fluids are slightly acid, alkaline solvents react with proteins in the skin. Most derivatives of ammonia (ammonium hydroxide, amides, amines) are highly alkaline and usually cause serious irritation and even skin burns upon direct contact.
3. Dehydration. Hygroscopic solvents such as the glycols absorb water and may eventually cause dermatitis due to skin drying.
4. Allergens and sensitizers. About 10 percent of the organic solvents in the Handbook are reported to be allergens or sensitizers, defined as chemicals to which certain individuals are abnormally sensitive on the first or subsequent exposure, respectively. Included in the allergens are turpentine, dimethylsulfoxide, benzyl alcohol, the three butyl alcohols and, though mild, the corresponding three butyl acetates. The sensitizers are epichlorochlorohydrin, ammonium hydroxide and tetraethylene pentamine.

In any event, all organic solvents can be expected to cause dermatitis sooner or later. The best way to avoid potentially troublesome skin problems is to minimize, or prevent altogether, direct contact with solvents through the use of protective creams or rubber gloves.

Eye Contamination. Contact of any foreign matter with the eyes is always a matter of major concern because of their great sensitivity and because impairment or loss of vision is so great a tragedy.

If accidentally splashed in the eyes, the typical organic solvent is certain to be painful and irritating at the very least, and many are capable of causing severe eye burns or permanent eye injury. The latter is most apt to be caused by the excellent degreasers and alkaline solvents mentioned in the previous section. Rather curiously, among the oxygenated solvents, many butyl and hexyl derivatives are prone to cause serious eye irritation even though they are not particular skin irritants.

Damage can be minimized by prompt action in washing out the eyes by emergency medical treatment. The simple preventative measure of wearing safety goggles is, of course, far preferable.

Irritation from Vapors. Besides skin and eye contact with the liquid, irritation of some form may be expected from exposure to solvent vapors. In most cases, mild irritation of the eyes and other mucous membranes may develop. On the other extreme are the solvents, notably the aforementioned alkaline compounds, where vapors are so irritating that they would not be voluntarily tolerated. There are also cases where chronic exposure to vapors has caused skin problems, serious lung irritation, and even internal organic injury. Examples are:

Methyl ethyl ketone - Skin dermatoses
Propylene oxide - Lung injury
Tetraethylpentamine - Asthma
Turpentine - Kidney injury.

Another class of irritants are the photochemically reactive solvents, which have already been mentioned several times during this conference. Such solvents may or may not be irritating by themselves, but they react with strong sunlight or other sources of ultraviolet light to form compounds that are definite irritants. As seen in table 2, only 17 of the 123 solvents in the Handbook are classed as photochemically reactive. These include all aromatic hydrocarbons except benzene, several ketones, two chlorinated hydrocarbons, and one alcohol, and are the ones involved in EPA emmision control regulations. All other solvents in the Handbook are currently "exempt."

Table 2. Photochemically reactive solvents

Class of photochemically reactive compound	Emission limitations (vol. percent)	Identity of solvent
Olefinic unsaturation	5	Furfuryl alcohol Ethylene dichloride
Aromatic hydrocarbons C8 and above except ethyl benzene	8	Xylene Naphtha (3) Turpentine
Ethyl benzene	20	Ethyl benzene
Ketones (branched hydrocarbon structure)	20	Methyl iso-butyl ketone Methyl iso-amyl ketone Ethyl sec-amyl ketone Di-iso-butyl ketone Diacetone alcohol Mesityl oxide Isophorone
Trichloroethylene	20	Trichloroethylene
Toluene	20	Toluene

CNS Depression

After skin dermatitis, the second most common complaint about organic solvents has to do with depression of the body's highly organized central nervous system (CNS). CNS depression is the usual result of acute overexposure to certain chemicals referred to as "narcotics." In industrial operations, it may occur from inhalation of excessive concentrations of solvent vapors for part or all of the 8-hour working day.

Examination of the list of symptoms in table 3 may help to understand better what CNS depression is. It should be noted that the symptoms are essentially the same as those which may develop from indulgence in alcoholic beverages. In like manner, the effects depend on the quantity absorbed in a given time period, the tolerance level of the particular individual, and the narcotic potential of the solvent.

Hydrocarbons, ethers, and oxides are the most powerful; as a matter of fact, some of these were once used or have been proposed as anesthetics in

Table 3. Depression of central nervous system

Symptoms:	Headache	Incoordination
	Dizziness	Weakness and fatigue
	Giddiness	Light anesthesia
	Mental confusion	Loss of consciousness
	Blurred vision	Death
Narcotic potential of solvents:		
	Hydrocarbons	Powerful
	Oxygenated	
	Alcohols	Weak
	Esters	Extremely weak (by hydrolysis)
	Ketones	Moderate (but hazard minimal due to irritant properties)
	Oxides and ethers	Powerful
	Glycol derivatives	Ineffective due to low volatility
	Other solvents	
	Chlorinated hydrocarbons	Powerful
	Nitroalkanes	Moderate
	NH compounds	Impossible due to potent irritant properties
Dangers:	Fatalities in confined spaces	
	Influence other bodily functions	
	Accident proneness	

medical operations. Esters are the weakest; CNS depression which results is caused by hydrolysis to the alcohol. It is also of interest that the irritating vapors of certain solvents serve as warning signals.

CNS depression is probably the most potentially dangerous form of toxicity for the following reasons:

1. It has caused a surprising number of industrial fatalities. Most of the cases involved workers who entered empty solvent vats or were trapped in confined spaces without respiratory protection. Under such circumstances, depression was so profound that respiration simply ceased.
2. Frequent or severe incidences cannot help but depress or influence other functions of the body. Many of you are aware that hexane, methyl ethyl ketone and methyl n-butyl ketone have been implicated in peripheral paralysis. The probable reason was a CNS-induced involvement of the autonomic nerve center in the brain, whereby the heart was ordered not to pump blood to the ends of the fingers and toes.

3. Examination of the list of symptoms indicates that, even in mild cases, a worker's well being and alertness are reduced; the inevitable result is increased accident proneness.

Every effort should be made to minimize incidences of CNS depression through adequate ventilation or appropriate respiratory devices.

Organic Injury from Cumulative Absorption

In previous sections, it was pointed out that irritant actions and CNS depression could both cause organic injury; however, this form of toxicity is more likely to result from the absorption of chemicals at a faster rate than they are eliminated. In industrial operations, the principal routes of absorption are vapor inhalation and skin contact. Considering that the lungs have an internal surface area of 100 square meters compared to 1-1/2 for skin over the entire body, it is obvious that vapor inhalation is the more significant route, especially with solvents having high vapor pressures. In either case, cumulative poisoning is extremely difficult to diagnose because it frequently takes years to develop recognizable symptoms.

Table 4 indicates that 44 of the 123 solvents in the Handbook are believed capable of causing organic injury from cumulative absorption. Case histories of adverse experiences in humans were uncovered for only 16 (refs. 5 and 6); as far as could be determined, the other 28 caused organic injury only in animals. To avoid misunderstanding, the Handbook labels the latter "possible cumulative poisons."

The most potent cumulative poisons in the Handbook are benzene, which attacks the blood-forming mechanism, and carbon tetrachloride, which injures the liver and kidneys. Both are highly volatile, and exposed workers should be given close medical supervision. Blindness has been caused by the vapors of methyl alcohol, and, as might be expected, by those of methyl acetate because it hydrolyzes to methyl alcohol. Most of the other solvents in the table have been implicated in liver or kidney injury.

There is currently no United States Occupational Exposure Standard (ref. 7) for two proven cumulative poisons having low vapor pressures: ethylene glycol, which caused kidney abnormalities after a year or two of exposure to heated vapors; and diethylene glycol n-butyl ethyl acetate, withdrawn from

Table 4. Organic injury from cumulative absorption

Chemical Family	Total \#	Capable \#	Proven \#	Identity	Vapor Pressure at 20° C mmHg	USOS 8-hr avg. ppm	TLV 8-hr avg. ppm
Hydrocarbons							
Aliphatic	3	0	-				
Aromatic	4	2	2	Benzene	74	10	25 (skn)[a]
				Xylene	5	100	100 (skn)
Distillates	5	3	1	Coal tar naphtha		100	
Oxygenated							
Alcohols	17	3	2	Methyl alcohol	97	200	200 (skn)
				Amyl alcohol	2	100	--
Esters (of alcohols)	13	2	2	Methyl acetate	170	200	200
				Amyl acetate	4	100	100
Ketones	15	3	0				
Ethers and oxides	7	5	1	Dioxane	29	100	50
Glycol derivatives							
Glycols	9	3	1	Ethylene glycol	0.05	--	100
Glycol ethers	24	9	2	Ethylene glycol methyl ether	6.2	25 (skn)	25 (skn)
				Ethylene glycol ethyl ether	4	200 (skn)	100 (skn)
Glycol esters	5	5	1	Diethylene glycol butyl Ether acetate	<0.01	--	100 (skn)
Other							
Chlorinated hydrocarbons	6	3	3	Carbon tetrachloride	92	10	10 (skn)
				Ethylene dichloride	62	50	50
				Perchloroethylene	14	100	100 (skn)
Nitroalkanes	4	4	0				
NH_x compounds	100	4	1	Dimethyl formamide	2.7	10 (skn)	10 (skn)

[a] (skn) = may be absorbed through vapor inhalation and skin contact.

the pesticide market because of harmful skin absorption. It should also be noted that existing USOS values, which take legal precedence at the Federal level, do not always agree with recommended TLV values (ref. 8). Many changes must be expected as a result of increased activity on the part of OSHA, NIOSH, and other agencies.

Oral Intake

Although oral intake of most solvents will invariably cause illness or death, this route is not considered a problem in industry as much as it is around the household, especially where children are concerned. There are, however, inadvertent opportunities for oral intake about which industrial workers should be aware. Swallowing may occur to a minor extent when deeply inhaling contaminated air. More serious amounts can be introduced into the body when breathing misted vapors, or when consuming food or drink which has become contaminated by exposure to vapors or by using hands or containers which contain solvent remnants. Every effort should be made to avoid such incidences.

Summary

Organic solvents have achieved importance in modern society and technology because they possess desirable performance qualities and attractive economic advantages. A summary of data compilations undertaken by the printing ink industry has demonstrated that the majority of solvents also possess properties associated with fire and health hazards. It is not the intent of the compilations to discourage use of any products, but rather to point out what the dangers are so that users may take effective preventive measures. The flammable and toxic potential of the typical organic solvent can be largely eliminated through adequate ventilation and prevention of skin contact.

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ANGIOSARCOMA OF THE LIVER AMONG PRINTERS

John T. Herbert, M.D.*

Abstract

Over the past several months, the Cancer and Birth Defects Division of the Center for Disease Control has been compiling a registry of all cases of angiosarcoma of the liver occurring in the United States from 1964-1974. Cases have come from death certificates via the National Center for Health Statistics, from the Armed Forces Institute of Pathology, and from direct correspondence with pathologists across the country. From the death certificates alone, five cases of angiosarcoma of the liver were identified as workers in the printing industry. Another three cases were found in printers as additional cases were reported. In light of the known association of vinyl chloride and angiosarcoma, and the fact that many printing inks use a vinyl chloride resin, special attention was immediately focused on this group.

Pathology of these eight cases was reviewed by Dr. Louis B. Thomas, Director of Pathology, National Institutes of Health, and Dr. Hans Popper of Mount Sinai School of Medicine, but only one of the original five cases was confirmed as angiosarcoma of the liver. Pathological review of the other three cases, along with epidemiologic findings of all eight individuals, is in progress.

Angiosarcoma is a very rare malignant tumor of the liver that we have been studying at the Center for Disease Control. How did we get involved with printers? I should say from the outset that this is a very preliminary report and that I received my last information by telephone about 20 minutes before the session began.

The Center for Disease Control (CDC) is establishing a registry of all cases of angiosarcoma of the liver occurring in the United States from 1964 to 1974. CDC became involved shortly after this tumor was recognized in plastics workers and linked to vinyl chloride exposure. We began setting up this registry to see if there were other industries and other chemicals that

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*Cancer and Birth Defects Division, Bureau of Epidemiology, Center for Disease Control, Atlanta, Georgia.

could contribute to the development of angiosarcoma of the liver. The center was involved in examining the records of the original plastic workers in B. F. Goodrich plants and several papers were published on this subject. Without question, vinyl chloride monomer has been recognized as causing angiosarcoma of the liver and other angiosarcomas in animals.

When the registry was set up, we arranged to get death certificate information on all cases of "miscellaneous liver tumors" from tumor registries and from the National Center for Health Statistics. We also sent out mailings to pathologists all over the country asking if they had seen cases of angiosarcoma of the liver.

Our purpose and goal was to identify all cases of angiosarcoma of the liver, regardless of the cause, and then to do some epidemiologic footwork and look for occupational histories with vinyl chloride exposure or exposure to other chemicals. I might point out that angiosarcoma has also been shown to be caused by exposure to arsenic and to thoratrast, which is a contrast media used in the 1940's for radiographic studies in hospitals.

We looked to see if there were other chemicals causing this tumor, and we also looked to see if there were other industries previously not known that were using any of these chemicals. When we began looking through the thousands of death certificates and receiving trickles of letters from pathologists, we noted a cluster of six cases of angiosarcoma, which were reported in printers. This was immediately quite striking.

Table 1 shows the incidences of angiosarcoma of the liver as estimated from the third National Cancer Survey; 0.014 cases per 100,000 should occur in the overall population. We estimated approximately 1 million printers, which may not be a precise figure. According to the International Printing Pressmen's Union (personal communication) two printers unions claim to represent approximately 30 percent of the printers in the country. By doing a little bit of arithmetic, I came up with 690,000 and I rounded it off to 1 million to try and bias the study against our findings.

Applying this rate to the 1 million printers, we would expect 1.4 cases over a 10-year period. We observed six cases in the period 1964 to 1974, and the first thing that came to our minds was that we had an epidemic of angiosarcoma in printers.

About this time we began our epidemiologic investigation. We made

Table 1. Observed and
expected number of cases among printers

Incidence - 0.014 cases/1000,000*

× 10^6 Printers**

Expected - 1.4 cases in 10 years

Observed - 6 cases, 1964-1974

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*Third National Cancer Survey.

**International Printing Pressmen's Union.

every attempt to trace the families of these individuals, usually through private physicians who signed the death certificate. We did get pathology slides and cell blocks for futher review and for confirmation on all cases. We sought a representative occupational and residential history, looking mainly for possible exposure to vinyl chloride monomer, since we know this caused angiosarcoma of the liver. Of course, we looked for other chemicals as well.

We were puzzled by the five initial cases of angiosarcoma in printers, and we had no reason to suspect that printers were using vinyl chloride, even though we know they were using a host of chemicals It was then brought to our attention from our colleagues at NIOSH that polyvinyl chloride, which has not yet been implicated as being carcinogenic, is used in the manufacture of certain printing inks. We also know that in many of the plastic end products of polyvinyl chloride, vinyl chloride monomer lies trapped within the polymers.

We then received notification of three additional cases, which brought our total to nine printers who had a diagnosis of angiosarcoma of the liver on their death certificates. We certainly were interested in this, and we arranged to get the slides. We looked for the occupational history on these people. I have summarized in table 2 our nine cases. The first five cases are the original five and the next three are the subsequent ones that came in.

All of these gentlemen had on their death certificates angiosarcoma of the liver or some of the synonyms that we use: malignant endothelioma, etc. They also had on the death certificates "Printer," or in one case,

Table 2. Angiosarcoma of the liver reported among printers, 1964-1974

Printer	Age at death	Years of exposure	Job description	Chemicals	Diagnosis local
1	50	25	Offset pressman	Inks, cleaning fluids	ASL
2	70	?	Offset pressman	Inks, cleaning fluids	ASK
3	84	50	Self-employed printer	Inks, cleaning fluids	ASL
4	71	35	G.P.O. printer	Inks, cleaning fluids	ASL
5	40	24	Linotype operator	Molten lead, inks, cleaning fluids	ASL
6	20	3	Assistant; cleaner	Inks, cleaning fluids	ASL
7	59	3 (25)	Printer (janitor)	Inks, cleaning fluids	ASL
8	61	16 (10)	Printing salesman (solvent mixer)	CCL_4	ASL
9	59	42	Pressman	Inks, benzene cleaning fluids	Malignant fibroxanthoma

"linotype operator," but all were people working in the printing industry.

When we conducted our epidemiologic investigation, we noted right away that some of these people were not really printers. If you look at case numbers six, seven, and eight, case number six was only exposed to these chemicals for 3 years and turned out to be a part-time printer and cleaning assistant in a print shop. Case number seven had been a janitor for the previous 40 years, and was promoted to a blueprint printer the last 3 years before he became ill. He had been exposed extensively to cleaning fluids, but again had only been a printer for 3 years.

Case number eight turned out not to be a printer at all, but a salesman for a print company, having minimal exposure to the printing industry itself, and case number nine was indeed a printer for 42 years, but the hospital diagnosis was fibroxanthoma of the liver. This case was referred to us because the original pathologists were unsure about the diagnosis. By telephone, there was a possibility that this may have been an angiosarcoma of the liver, but on pathologic review it was not. We were left with the first five cases. When the pathology on these cases came to our attention, we immediately sent them to Dr. Louis B. Thomas and Dr. Hans Popper at the NIH to review all of our slides. They have had the opportunity to review almost every case of angiosarcoma of the liver that has been reported, and Dr. Popper, of course, is a liver pathologist well known all over the world. On review by Drs. Thomas and Popper, only case number five was an angiosarcoma.

By this time, EPA contacted us and wanted a statement on the rash of angiosarcoma cases that we had been studying in printers. The study was preliminary at that time and we felt that we had to have pathologic confirmation before we could report any more cases of angiosarcoma.

In summary, on reviewing our nine printers, only one of them turned out to have angiosarcoma of the liver. This is not to be critical of the local hospitals; it should be pointed out that this is a very difficult diagnosis to make. The diagnosis is usually best made following death, when the entire liver is available. We only expect one out of 10 million deaths to have this diagnosis, and most pathologists just do not see this tumor.

I do not have the final report on the other cases, but we can tell you that case number five was the only printer with angiosarcoma of the liver. I intentionally rushed over cases six and seven. They are believed to be angiosarcoma of the liver, but with that short, recent exposure, we cannot implicate chemicals in the printing industry. We expect to have a final report on all of these cases with the conclusion of the angiosarcoma registry.

DISCUSSION

CHAIRMAN SCHAEFFER: A question has been asked, which one was the one?

DR. HERBERT: The one out of five is case number five. He was a linotype operator for approximately 24 years. He was exposed to molten lead and the other chemicals that go into linotype operations. But he also worked in a printing company that was a large warehouse-type of job shop. All of the printing and everything else was done in the same room.

JEFFREY D. BOEHLERT (Sun Chemical Corporation, Carlstadt, New Jersey): Is there not arsenic in molten lead?

DR. HERBERT: Well, we asked about that because of the purity of the lead. I think there is. The fact is that we have no proof to even guess what his exposure to arsenic was. I am certain all linotype operators have had a similar exposure.

I would just say that we just cannot make that statement at this point. But there is some evidence that all of these chemically induced angiosarcomas of the liver, certainly all of the vinyl chloride workers, and probably the arsenic workers have a certain pattern to their histology. When you review these tumors under the microscope, the tumor arises from, I believe, the endothelio cell walls. And as Dr. Thomas and Popper have pointed out, this is not characteristic of the "spontaneous angiosarcoma," as previously reported.

CHAIRMAN BURACHINSKY: I just wonder whether you have ever consulted with the particular printing ink firm involved, which would probably pinpoint for you rather quickly whether any vinyl chloride was used. It is fact that only about 1 percent or less of printers use vinyl chloride at all. Very few inks are being made with vinyl chloride. So you probably won't...

DR. HERBERT: The answer to your question is yes. We contacted five different companies and I think manufacturers in the Atlanta area, two in the Massachusetts area. No one really knew of vinyl chloride being used in the prints any more. I only cited the reference from the book because it was pointed out that it is there, and there was a possibility of exposures.

DR. HERMAN F. KRAYBILL (National Cancer Institute, Bethesda, Maryland): As you said earlier, there is a possibility for the PVC monomer leaking out and there is concern about PVC monomer where you have PVC stored. I was going to ask if it were true that there was PVC present--whether there was any monitoring that took place? Second, have you looked at any structural analogs of viny chloride?

DR. HERBERT: We have not directly, but other investigators have looked at them. I think possibly people from NIOSH might be a little bit better qualified to answer that question than I am. But certainly in the rubber industry, with some of the synthetic rubbers, there are structural analogs. And vinyl chloride has been reported in rubber work. Excuse me. Angiosarcoma has been reported in rubber workers.

MR. RAY NEFF (Department of Health and Safety, Indiana State University, Terre Haute, Indiana): This does not have anything to do with the printing industry. What was the average exposure for the cases that have to do with PVC? Was it pretty long exposure or short exposure? Could you expect, say, a 3-year exposure to trip-off or cause angiosarcoma?

DR. HERBERT: In the cases reported on the original vinyl chloride workers, and I believe most of the subsequent workers, there was certainly a longer exposure than this. People like to say that it takes 15 to 20 years. Of course, the duration of exposure and the dose and latency are things that have to be reckoned with. I believe the tumor has been reported in people who worked less than 15 years. But the tumor did not arise until 20 years after their exposure. So I cannot answer that question directly, except that 3 years of exposure with no prior exposure certainly would be unusual. This is not what has been seen in the plastics worker.

DR. KINGSLEY KAY (Mt. Sinai School of Medicine, New York): May I ask what was found out about the cleaning fluid used by the linotype operator?

DR. HERBERT: We asked the company where he worked and everybody kept telling us benzene, although we were informed that benzene is no longer used. So we presumed that it may have been one of the many solvents being used in the industry now--I cannot tell you exactly what it was, but we were assured that it certainly was not benzene.

DR. KAY: May I say that in the survey I did, the current solvents used to clean typeface and in proofpulling were methylchloroform and methylene chloride, and they are of great interest because methylchloroform is a cardiac sensitizer, and methylene chloride converts to carbon monoxide in the body. These are things we now know.

They were, of course, widely used because they were pushed as substitutes for carbon tetrachloride and trichlorethylene. And all the men on your list in the 20-year category, have been using carbon tetrachloride. The older ones have been using benzene, and the newer ones have been using trichlorethylene, methylene chloride, and methylchloride almost without any question of doubt, because there is nothing else that works.

DR. HERBERT: I might point out that one case of angiosarcoma that has carbon tetrachloride exposure indicated was not a printer, but he manufactured this stuff in his basement. And for over 15 years, he made solvents out of a carbon tetrachloride base.

THE FLOOR: I am just wondering where Dr. Kay got his information, because there may have been one or two people who may be using methylchloroform, but very few people will be using carbon tetrachloride, methylene chloride, and methylchloroform as a basic wash. It may be used to lift the flash point, but essentially they are what we called benzenes. They are the petroleum aliphatic solvents that are used for cleaning linotype.

DR. KAY: Well, I did not see anybody using carbon tetrachloride. What I said was, I was told that carbon tetrachloride had been used many years ago, and had been replaced with these two solvents.

CHAIRMAN SCHAEFFER: Are there any other questions?

MR. CHARLES WARNER (National Cancer Institute, Bethesda, Maryland): I wonder if we are not going to change the health picture considerably by forcing printers to go to nonphotochemically active solvents. I wonder if we should not proceed more carefully in light of the fact we may cause a considerable industrial hygiene problem.

CHAIRMAN SCHAEFFER: Dr. Herbert, any comment?

DR. HERBERT: My only answer to that would be to clean them by machine. I do not know enough about the printing industry to even attempt to answer that question.

CHAIRMAN SCHAEFFER: I think the point that is made is a very interesting one, because one has to look at what the possibilities are in any new system that is developed for the industry. And we are talking new systems very frequently, including the cleaning operations.

LITHOGRAPHY: LABORATORY EVALUATION OF ENVIRONMENTAL RISK

Robert L. Bohon, Ph.D.*

Abstract

This paper addresses the problem of estimating the potential environmental hazard of lithography from data on the entry level and biological impact of waste materials from the plate and press rooms. Examples of ecosystem reservoirs and pathways are related to existing disposal methods for spent developers, printing inks, driers, fountain solutions, blanket washes, paper, and discarded press blankets and plates. A laboratory classification scheme similar to that proposed by the National Academy of Sciences is used to assess possible environmental hazards from laboratory-scale tests as well as information contained in the literature on the volume and dispersal of these waste materials. From these considerations it is concluded that under normal use conditions lithography poses a very minor environmental hazard.

INTRODUCTION

The prediction of potential environmental hazard for any given product or chemical compound eventually becomes an attempt to extrapolate the results of short-term tests or observations to very long-range effects in an ever-changing, complex real-world system. How can we efficiently utilize environmental toxicological data, in conjunction with expected use and disposal information, to estimate the potential environmental impact of a given product or process?

Today I will present a brief outline of an assessment of the potential environmental hazard associated with the practice of lithographic printing, especially as it relates to the waste materials from the plate and press rooms. The methods routinely used at 3M Company for such an assessment on new or modified products closely parallels the suggested protocols of the National Academy of Sciences, and I shall frequently refer to their recent report (ref. 1).

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*Manager, Environmental Laboratory, Environmental Engineering and Pollution Control Division, 3M Company, St. Paul, Minnesota.

We shall first discuss ecosystem models and our present state of knowledge as to how chemicals move within them. Consideration will be given to those properties of a compound which control its availability to living systems, as well as to laboratory methods of measuring and predicting biological toxicity and impact. Finally, the lithographic printing process will be briefly outlined, the wastes from the plate and press rooms identified, and an assessment made of the environmental impact of each, using the concepts of entry level and biological impact.

ECOSYSTEMS AND CHEMICAL MOVEMENT

Figure 1 illustrates the dynamic system of reservoirs and pathways for chemicals in the global environment (ref. 1). Atmospheric residence times vary from weeks for small particles to years for gases. It takes 2 to 4 weeks for particles to circumnavigate the earth in midlatitudes, 3 to 6 weeks near the equator. As one might expect, residence times in the ocean vary from a century (iron, aluminum, or titanium particles) to hundreds of millions of years (sodium) and depend upon the chemical nature of the substance. Refractory organic materials have oceanic half-lives of thousands

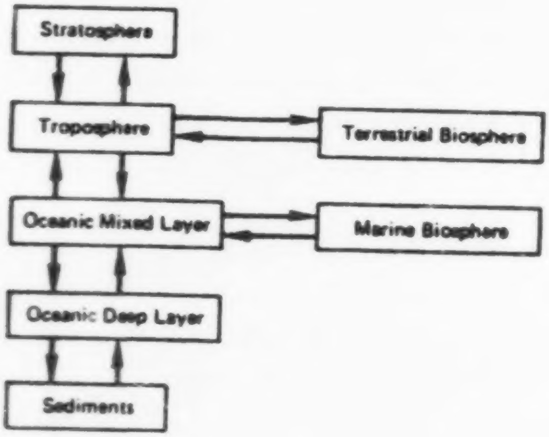

Figure 1. Reservoirs and pathways of chemicals in the environment (ref. 1, p. 62).

of years, and mixing times range between several hundred years in the Atlantic to a thousand years in the Pacific for materials introduced into the deep layers. Most dissolved substances pass through the mixed layer in a matter of years, or a decade at the most.

When an effort is made to model a dynamic system in an aquatic environment, a very complex, interrelated set of variables must be considered. A pictorial illustration of such a model by Chen and Orlob (ref. 1) is shown in figure 2. For each cell there are 23 differential equations, one for each environmental variable: temperature, total dissolved solids, biochemical oxygen demand, pH, elemental concentrations (C, N, P, etc.), plus a variety of biological variables (biomasses of algae, zooplankton, cold-water and warm-water fish, benthos feeders), and mass balance effects due to processes such as advection, diffusion, settling, inflow, outflow, decay, chemical transformation, biological uptake, respiration, growth, mortality, and grazing.

It is apparent that mathematical modeling of the flow and concentration

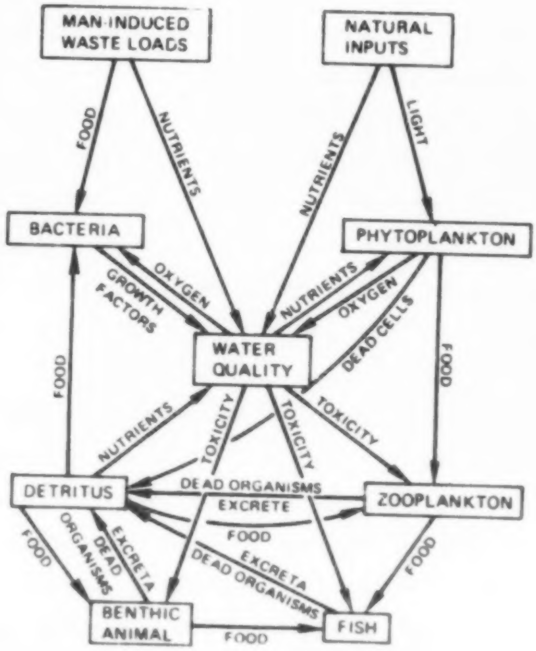
MAN-INDUCED WASTE LOADS
NATURAL INPUTS
FOOD
NUTRIENTS
NUTRIENTS
LIGHT
BACTERIA
PHYTOPLANKTON
OXYGEN
GROWTH FACTORS
NUTRIENTS
OXYGEN
DEAD CELLS
WATER QUALITY
FOOD
FOOD
NUTRIENTS
TOXICITY
TOXICITY
TOXICITY
DETRITUS
DEAD ORGANISMS
EXCRETE
ZOOPLANKTON
FOOD
FOOD
DEAD ORGANISMS
EXCRETA
EXCRETA
DEAD ORGANISMS
FOOD
BENTHIC ANIMAL
FOOD
FISH

Figure 2. Definition of an ecosystem (Chen and Orlob, 1972)(ref. 1, p. 350).

distribution of substances in the environment is a difficult and complex business. Nevertheless, the danger or hazard associated with either naturally occurring or synthetic chemicals depends upon not only their biological impact, but also upon their distribution in the environment. A hundred pounds of salt dumped on my lakeside back yard would have disastrous ecological effects, whereas the city maintenance department routinely spreads tons of salt on our St. Paul city streets with currently acceptable side effects, thanks to containment and high dilution by natural precipitation.

In considering the movement of compounds through the environment and their availability to living organisms, the following indicators of movement are important (ref. 2):

- vapor pressure,
- water solubility,
- octanol-water partition coefficient, and
- soil adsorption/leaching behavior.

As a first approximation, vapor pressure will be related to entry into the atmosphere, water solubility will control entry into an aquatic ecosystem, and the octanol-water partition coefficient will be a good indicator of the potential for bioconcentration.

Such properties as reactivity with oxygen and water, photodegradation and tendency toward smog formation, microbial degradation and transformation, and metabolism by plants and animals are indicators of persistence in the environment. Note particularly that one must be concerned not only about the parent compound, but also the amount, location, and biological impact of materials generated from the parent compound by the environment itself.

J. M. Wood and coworkers have published widely on the biological mechanisms by which toxic elements are cycled in the environment (ref. 3). The mercury cycle is shown in figure 3 and illustrates the way in which sedimentary microorganisms and enzymes convert inorganic mercury compounds at a pH of about 4.5 into the deadly poisonous neurotoxin, methyl mercury, which in turn is readily soluble in lipids and can bioconcentrate in fish. The same process also produces dimethyl mercury (but at a rate 6,000 times slower), which is volatile and photolyzed by UV light to metallic mercury plus methane and ethane.

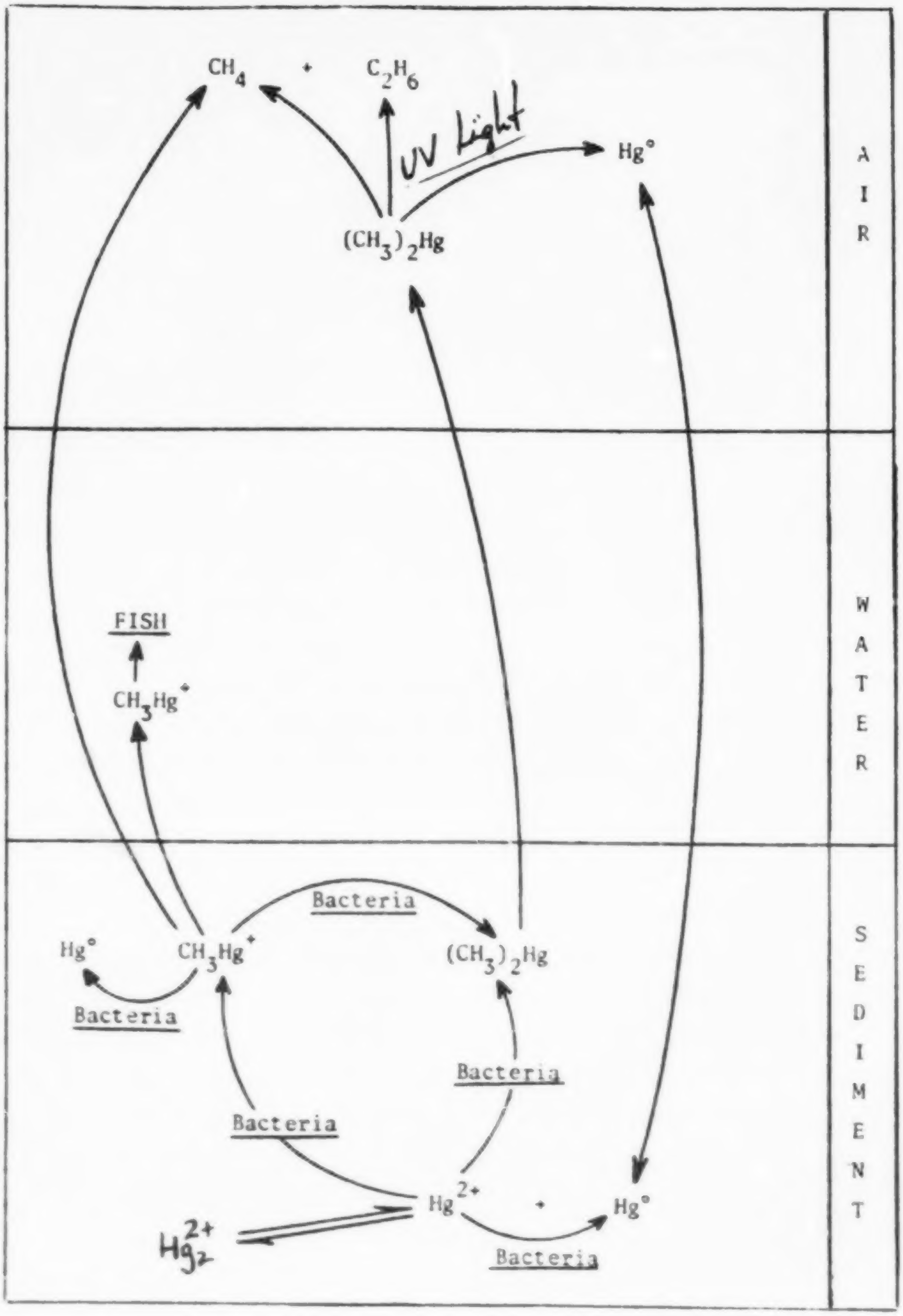
CH_4 + C_2H_6
UV Light
$Hg°$
$(CH_3)_2Hg$
AIR
WATER
SEDIMENT
FISH
CH_3Hg^+
Bacteria
$Hg°$
CH_3Hg^+
$(CH_3)_2Hg$
Bacteria
Bacteria
Bacteria
Hg^{2+} + $Hg°$
Hg_2^{2+}
Bacteria

Figure 3. The mercury cycle (ref. 3).

Table 1. Classification of elements according to toxicity (Wood, ref. 3)

Noncritical			Very toxic and relatively accessible			Toxic but very insoluble or very rare	
Na	C	F	Be	As	Au	Ti	Ga
K	P	Li	Co	Se	Hg	Hf	La
Mg	Fe	Rb	Ni	Te	Tl	Zr	Os
Ca	S	Sr	Cu	Pd	Pb	W	Rh
H	Cl	Al	Zn	Ag	Sb	Nb	Ir
O	Br	Si	Sn	Cd	Bi	Ta	Ru
N				Pt		Re	Ba

From such biological cycle considerations, Wood has suggested three classifications for toxic elements: (1) noncritical; (2) toxic and relatively accessible; (3) toxic, but very insoluble or very rare (see table 1).

It is evident that small disturbances in these dynamic cycles will affect the natural equilibria for any given element, which in turn will affect the concentrations of toxic intermediates. We are then faced with the problem of deciding which species of a toxic element should be monitored in the environment since chemical, physical, and biological transformations can have such a profound effect upon the movement and impact of any given element across boundaries in the biosphere.

Similar arguments apply to organic compounds, and again the persistence, concentration distribution, and transformation processes are important in assessing the environmental impact due to introduction of a given volume of some chemical compound into a biogeocycle at a given time and place. You are all familiar with the classic case of such synthetic refractory organics as polychlorinated biphenyls, for which mother nature has not yet developed mechanisms for detoxification at rates sufficiently high to prevent an adverse environmental impact through bioaccumulation.

ASSESSMENT OF ENVIRONMENTAL HAZARD

As mentioned previously, the environmental hazard of a given material depends not only upon its inherent biological impact (e.g., toxicity), but

Table 2. Scheme for classification of chemicals according to biological impact and dispersal (national or regional problems) (ref. 1, p. 227)

Entry level		Biological impact		
Dispersal	Volume	High (1)	Medium (2)	Low (3)
(1) Widespread	High release	1	2	3
(2) Widespread	Low release	2	4	6
(3) Localized	High release	3	6	9
(4) Localized	Low release	4	8	12

NOTE.-Low number indicates high priority.

also upon its volume and distribution in the environment at any given time. Table 2 presents a scheme for classification of chemicals according to these three parameters on a national or regional basis (ref. 1). I have taken the liberty of combining "dispersal" and "volume" under the general heading of "entry level," which indicates the combined effects of these two environmentally significant variables. A material with high biological impact and high entry level would have a top priority rating for environmental concern, whereas a low-entry-level, low-biological-impact material would receive a low priority rating.

Table 3 illustrates the factors contributing to biological impact and includes such items as toxicity, the importance of the receptor organisms, the scope of the ecological effect (with large-scale and chronic effects more serious from a testing standpoint than acute effects), the availability to organisms, the potential for biomagnification, and the stability or persistence of the compound.

In conjunction with the physical and chemical properties of a compound, application of tables 2 and 3 permit a preliminary assessment of environmental hazard and an objective decision on whether additional laboratory tests are necessary for reasonable predictions. Figure 4 is a suggested flow diagram for regulatory decisionmaking (ref. 1). Steps 3, 4, and 5 involve increasingly complicated and expensive laboratory and field testing, such as now required in varying degrees for pesticides and drugs. This scheme implies that we can make a reasonable estimate of environmental hazard

Table 3. Factors contributing to biological impact (ref. 1, p. 227)

	Level of importance		
Factor	(1)	(2)	(3)
Toxicity	High	Medium	Low
Receptor importance	High	Medium	Low
Type of effect	Interference with ecosystem functioning	Chronic effects at level of the individual	Acute effects at the level of the individual
Availability to organism	High	Low	
Potential for biomagnification	High	Low	
Stability and persistence	High	Low	

NOTE.-Low number indicates high significance.

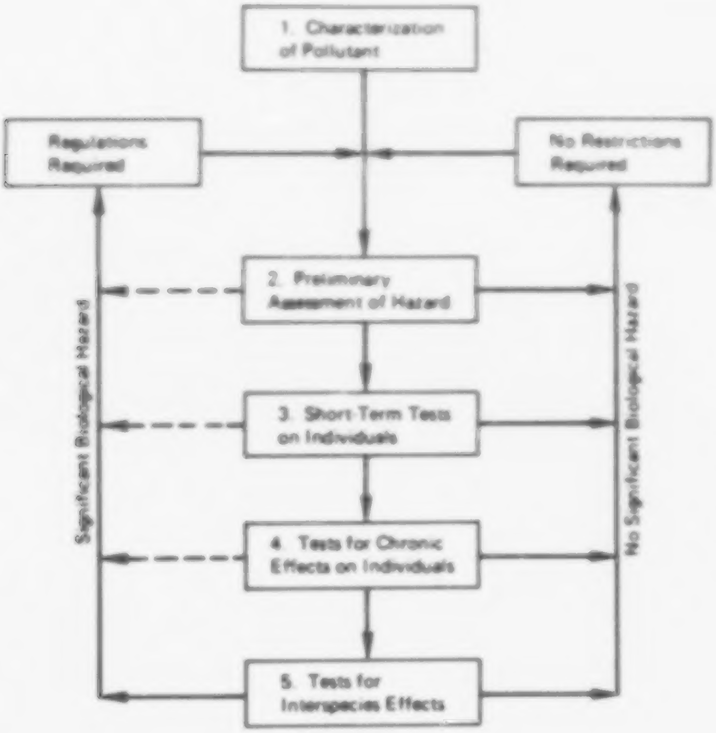
1. Characterization of Pollutant
Regulations Required
No Restrictions Required
2. Preliminary Assessment of Hazard
3. Short-Term Tests on Individuals
4. Tests for Chronic Effects on Individuals
5. Tests for Interspecies Effects
Significant Biological Hazard
No Significant Biological Hazard

Figure 4. Flow diagram for laboratory investigations of hazard (ref. 1, p. 225).

from a consideration of entry-level information and laboratory or field tests on biological impact:

Hazard = f (entry level, lab tests, field tests).

Furthermore, the degree of testing sophistication required and the extent thereof will be a function of both the anticipated biological hazard and the social gain expected from use of the substance:

Testing extent = f (biological hazards, social gain).

The more subtle biological effects, especially those observable only over spans of many years, present particularly difficult cases where fundamental data all too frequently are missing.

Step 3 of the suggested laboratory investigation scheme involves short-term tests on individuals and ranges from tests of a few hours to a couple of weeks. Table 4 summarizes some of the tests which should be included in this phase of evaluation.

If the results of short-term tests indicate the need for chronic tests, long-term indicators such as weight gain, food consumption, longevity, behavioral response, reproductive effects, and chenges in plant populations must be considered (step 4). For example, accumulative chemicals can sometimes be sequestered harmlessly in storage sites and later

Table 4. Short-term tests on individuals
(ref. 1, p. 227)

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*Toxicity and tendency for accumulation in organisms.
  Plants: seed germination, photosynthesis, transpiration.
  Animals: rates of ventilation, heartbeat, oxygen consumption.

*Rates of degradation and transformation.
  Short-term bioassay with fish.

*Analysis of body burdens before and after exposure.

No additional testing required if:
  rapid degradation,
  decomposition products of low toxicity,
  minimal bioconcentration,
  low entry level rating.

Additional testing required if:
  toxic chemical or decomposition products that are persistent,
  tendency to accumulate within an organism, or are of high toxicity.

released at toxic levels upon utilization of the store (DDT in fat or lead in bone). Long-term tests, of course, become expensive and time-consuming, and can only be justified when reasonable hazard is suspected.

Experience has shown that persistent toxic chemicals which can accumulate and be magnified in the food chain must be tested for much more subtle ecological effects (step 5), such as plant-plant interactions, productivity, plant-animal relationships, transport through food chains, and alteration by chemical or microbial activity.

R. L. Metcalf (ref. 4) has developed laboratory-scale microcosms containing several species at different trophic levels as a model for studying biodegradability and ecological magnification of radio-tagged chemicals (see figure 5). Radiotracer studies are limited, of course, to tracing only the tagged portion of a molecule, and following the decomposition products from complex parent molecules can sometimes prove confusing.

Finally, from a very practical standpoint, we are interested in the acceptability of a material into our existing waste disposal systems without upset or undue strain. For wastewater streams, treatability can be determined by biochemical oxygen demand (BOD) tests, which are an index of loading on secondary waste treatment systems or surface waters, and by BOD/COD* ratios, which indicate the degree of biodegradability. Nondegradable or difficulty degradable materials will pass unmodified through treatment

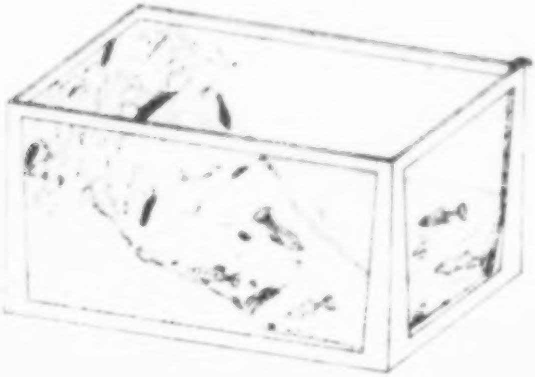

Figure 5. Model ecosystem for studying pesticide biodegradability and ecological magnification (ref. 4).

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*Chemical oxygen demand.

systems and into surface waters, or be landfilled or incinerated with the sludge.

LITHOGRAPHY

The lithographic printing process is based upon the ability to form oleophilic-hydrophilic images on a plate surface, which in turn permits differential adsorption of oil-base ink and subsequent transfer of the image to paper, plastic, cardboard, metal, etc. (see figure 6). Lithography accounts for almost 55 percent of all commercial printing in this country, has an annual growth rate of about 10 percent, and has doubled in dollar volume in less than 10 years. About half of all lithographic printing is general commercial work and advertising printing (about $1 billion each); the balance consists of labels and wrappers, catalogs and directories, financial and legal printing, and approximately $1/2 billion that is unidentifiable by product (ref. 5).

Within the commercial printing business, over 80 percent of the plants are small, employing less than 20 people and accounting for about 25 percent of the total dollar output. Plants employing over 250 persons account for an additional 25 percent of the business, and the remaining 50 percent of commercial printing is handled by plants with 20 to 250 employees (ref. 5). In total, there are approximately 8,400 commercial lithographic printing plants* and tens of thousands of "captive," or in-house, plants (ref. 6).

As might be expected, the growth in sales of offset inks (9 percent) has closely paralleled the growth of the offset printing industry. Offset

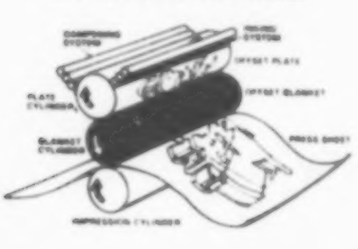

Figure 6. The lithographic process.

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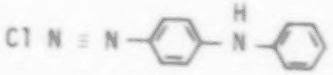
*Excludes job printers and 10"-plate industrial graphic printers.

ink accounted for 31 percent of the total ink sales in 1973 (ref. 7). A comparison of the 1967 and 1972 Census of Manufactures shows that the volume of lithographic and offset inks grew from 80.1 to 159.3 million pounds in 5 years (ref. 8).

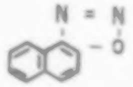
We shall restrict our environmental hazard discussion to the wastes generated in the plate processing and press rooms and ignore waste produced during the manufacture of lithographic supplies or the use and ultimate disposal of the final printed product.

After UV light exposure of a plate to a film negative, developing solutions are applied to remove nonlightstruck areas, producing a surface with both hydrophobic and hydrophilic areas. Developers for negative working plates are typically acidified aqueous solutions or emulsions of isopropanol, gum arabic, and synthetic lacquer resins (ref. 9). Negative-working presensitized plates may be coated with light-sensitive prepolymers, light-sensitive diazo resins made from such materials as 4-diazo-1, 1-diphenylamine



and paraformaldehyde, resin binders, small amounts of organic acids, organic or inorganic pigments, and indicator or sensitizing dyes.

Positive-working plates contain many of the same or similar materials, but the diazo materials are usually light-sensitive compounds such as 1-diazo-2-naphthol



which, upon exposure to light, give off nitrogen gas forming indene carboxylic acid. This compound is soluble in water solutions containing an alkaline material and permits removal of exposed areas with appropriate developers.

Development of lithographic plates, therefore, may produce the following waste materials in the plate room (see figure 7):

1. Developers
    a. Acidified aqueous solutions (negative plates): isopropanol, gum arabic, and synthetic lacquers.
    b. Caustics (positive plates)

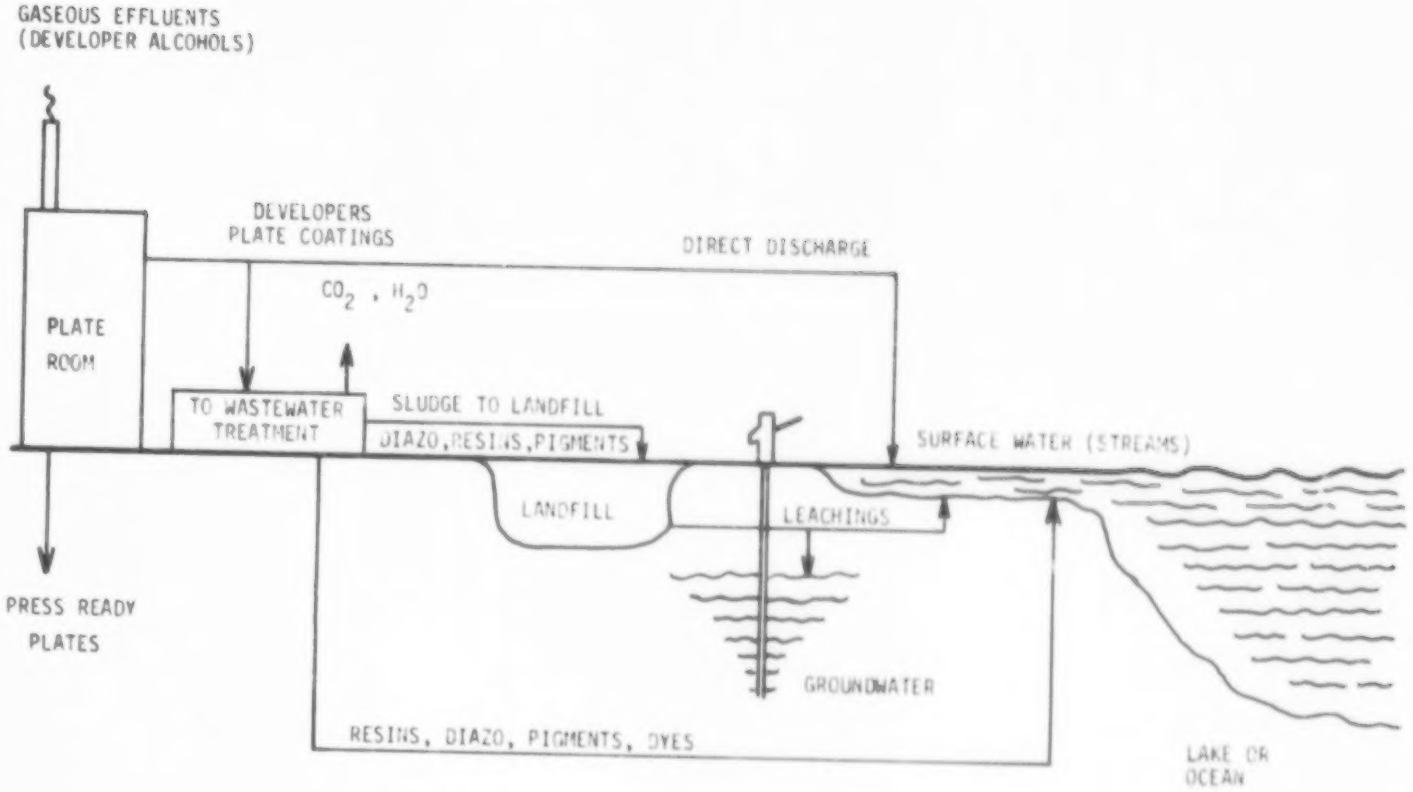

GASEOUS EFFLUENTS
(DEVELOPER ALCOHOLS)
PLATE
ROOM
DEVELOPERS
PLATE COATINGS
DIRECT DISCHARGE
CO_2 , H_2O
TO WASTEWATER
TREATMENT
SLUDGE TO LANDFILL
DIAZO,RESINS,PIGMENTS
SURFACE WATER (STREAMS)
LANDFILL
LEACHINGS
PRESS READY
PLATES
GROUNDWATER
RESINS, DIAZO, PIGMENTS, DYES
LAKE OR
OCEAN

Figure 7. Flow diagram of plateroom wastes.

2. Plate coatings
   a. Dyes
   b. Photopolymers
   c. Binders and resins
   d. Pigments
   e. Organic acids.

Volatile solvents such as alcohols will evaporate to a limited extent during plate development, but virtually all other wastes have the potential of entering the plant wastewater system and traveling through a municipal treatment system, individual septic system, or being discharged directly to surface waters. Water-insoluble polymers will, in general, be only slowly degraded and hence persist; the remaining waste materials, with the possible exception of certain pigments, will be biodegradable and relatively quickly returned to their respective natural cycles.

In the press room (ref. 10) we are confronted with a more complex system (see figure 8). During the printing process itself, alcohols and hydrocarbons will evaporate from the dampening system and ink fountains at the press, and in the case of offset printing with heat-set ink, also in the drying oven. Some plants utilize pollution control systems on the drying ovens to reduce the entry of hydrocarbon volatiles into the atmosphere, in which case ultimate disposal is either by afterburning reuse as forklift fuel, or in some cases recycling as an ink solvent.

The washup and cleaning solvents and ink fountains will introduce hydrocarbons into the overall volatile emissions from the plant. Some of these compounds fall into the class of photochemically reactive and hence contribute to the potential production of smog. Such emissions are already controlled by Rule 66 type regulations, which in turn vary from location to location throughout the country. There are lesser amounts of other oxygenated or chlorinated solvents released to the atmosphere, most of which are classed as nonphotochemically reactive.

Other wastes from the press room that must be considered find their way into landfills or incinerators via trash-handling systems (see figure 9):

- Waste paper, both with and without ink and other solids from ink and dampening systems;
- Discarded press blankets (rubber and fabric);
- Rags from cleanup operations, containing solvents and dissolved solids.

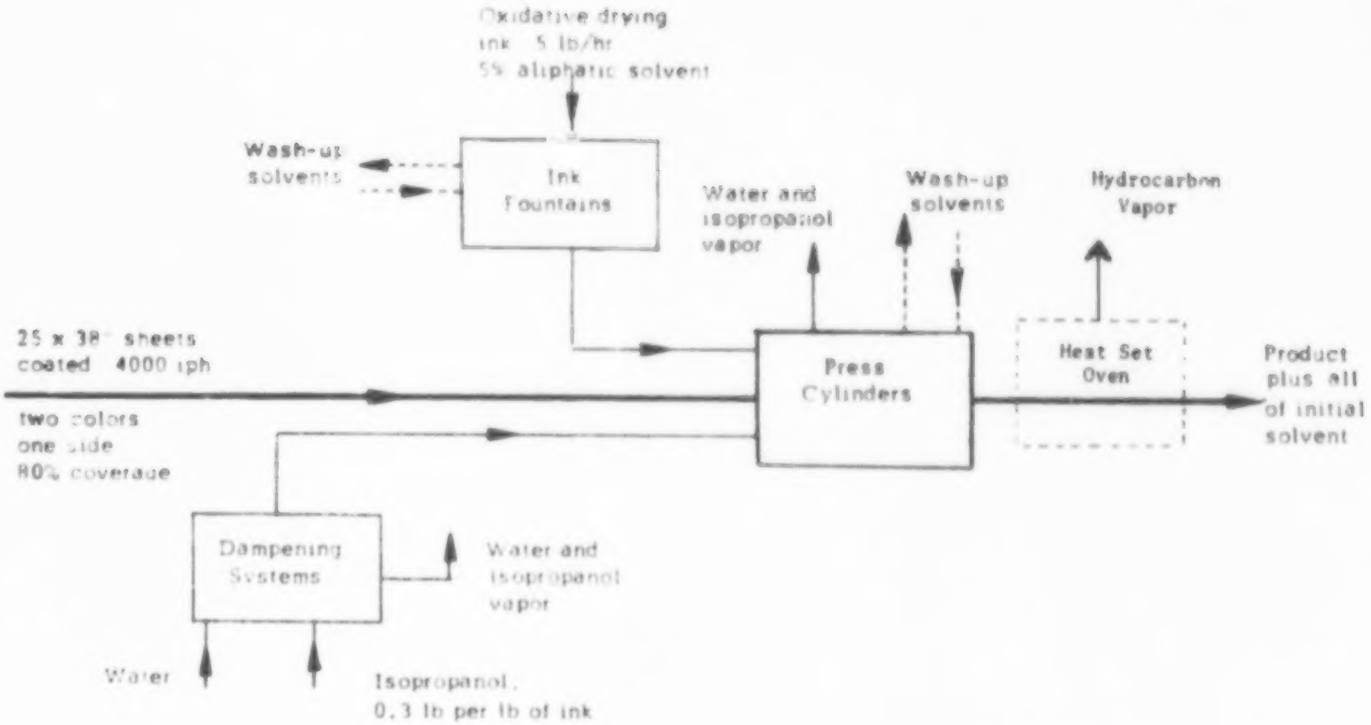

Oxidative drying
ink 5 lb/hr
5% aliphatic solvent
Wash-up
solvents
Ink
Fountains
Water and
isopropanol
vapor
Wash-up
solvents
Hydrocarbon
Vapor
25 x 38" sheets
coated 4000 iph
two colors
one side
80% coverage
Press
Cylinders
Heat Set
Oven
Product
plus all
of initial
solvent
Dampening
Systems
Water and
isopropanol
vapor
Water
Isopropanol,
0.3 lb per lb of ink

Figure 8. Sheet-fed offset--press room (ref. 10).

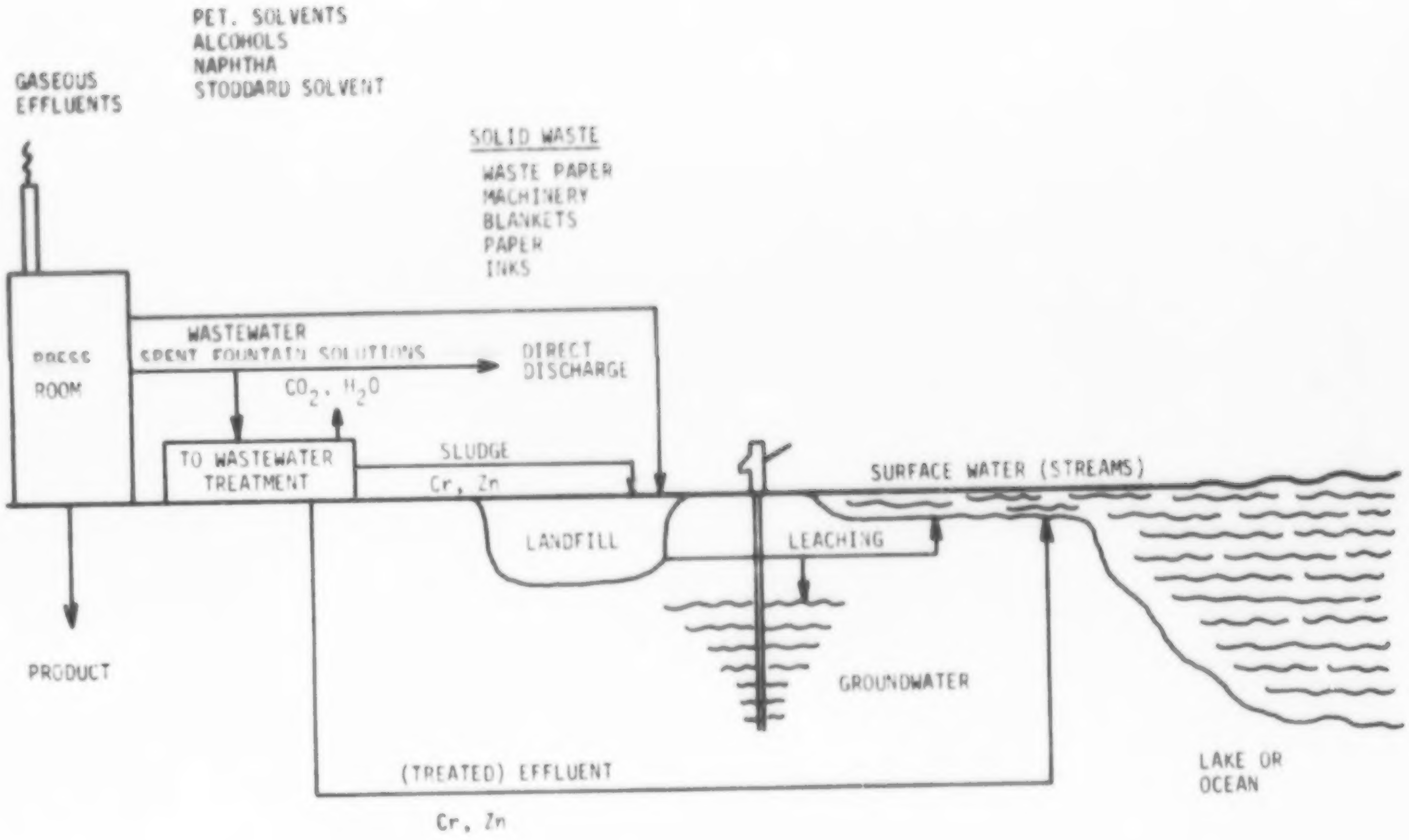

PET. SOLVENTS
ALCOHOLS
NAPHTHA
STODDARD SOLVENT
GASEOUS
EFFLUENTS
SOLID WASTE
WASTE PAPER
MACHINERY
BLANKETS
PAPER
INKS
PRESS
ROOM
WASTEWATER
SPENT FOUNTAIN SOLUTIONS
DIRECT
DISCHARGE
CO2, H2O
TO WASTEWATER
TREATMENT
SLUDGE
Cr, Zn
SURFACE WATER (STREAMS)
LANDFILL
LEACHING
PRODUCT
GROUNDWATER
(TREATED) EFFLUENT
Cr, Zn
LAKE OR
OCEAN

Figure 9. Flow diagram of press-room wastes.

Used plates are generally recycled to an aluminum fabricator.

The inks constitute a complex array of chemical compounds, including a wide variety of inorganic and organic pigments, oil resins, vehicles, and driers. The fountain solutions contain dissolved solids which mostly are carried over onto the final printed product (some of which is waste). Perhaps 20 percent of the solutions are dumped down the drain at the end of a week's run. This liquid waste includes organic acids, ammonium dichromate, zinc nitrate, and gums.

LITHOGRAPHIC WASTE ENTRY LEVELS

With this background on ecosystem modeling, on an enumeration of the lithographic processing waste materials, and on some laboratory indicators for biological impact, we now need to summarize the volumes and dispersal characteristics in order to assess entry levels. This information, plus biological impact estimates, will permit an estimate of potential environmental hazard for each waste material, as well as emphasizing where additional data are needed for an intelligent assessment.

The following tables summarize U.S. information on each type of lithographic waste material, arranged according to:

route of disposal

↓

entry level

↓

biological impact

↓

ultimate sink

↓

estimated environmental hazard.

The tables are further grouped according to the general class of waste material: inks, plate coatings, fountain solutions, and other.

The disposal route for any given material will be an important factor in predicting its entry level into the environment. The entry level, combined with information on biological impact, permits some evaluation of the ultimate environmental sink for the material and, finally, an assessment of environmental hazard.

It is obvious, of course, that there are missing data, and we can only make an educated guess for many of the formulations included under the broad range of chemicals used somewhere in the lithographic printing process.

Although we have very little specific information on the biological impact of some of the proprietary pigments, indicator dyes, and light-sensitive polymers used in plate coatings, it is apparent that the volumes discharged from the plate room processing steps are extremely small and constitute very little problem as shown in table 6.

A glance at table 7 on inks illustrates that the pigments and driers include heavy metal components that we know to be potentially detrimental to the environment.* It is also clear that the total levels of ink used for lithography run into millions of pounds and are therefore of obvious concern to our overall environment. We estimate, however, that less than 10 percent of the ink components are discharged as waste from the press room, the remainder leaving the plant in the form of finished product. In all cases, the inks eventually enter the biosphere through either incineration or landfilling of printed matter on an exceptionally widespread distribution level. For proper assessment on a global basis, additional information on biological impact of ink components will be necessary.

The solids contained in fountain solutions are largely deposited on the finished product, and probably less than 20 percent is dumped down the drain. Table 5 shows that the quantities are very small indeed, and the major environmental concern is with atmospheric discharge of vapors, as discussed previously.

Table 8 includes data on various other components used in lithography, as well as a recapitulation of total organic liquid use (solvents and ink components), which we have discussed before.

Table 9 summarizes the potential environmental hazard of these materials and emphasizes the necessity of good waste management for materials with significant biological impact, especially heavy metal compounds.

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*Carbon has been omitted from consideration as an environmentally significant constituent, although carbon blacks are known carcinogens due to benzene-soluble aromatic hydrocarbon components (Kingsley Kay, "Toxicological Evaluation of Chemicals Used in the Printing Inks Industries," this conference).

Table 5. Fountain solutions
(1,500,000 gal/yr – U.S. usage in litho)

		Gum	Phosphoric acid	Ammonium dichromate	Zinc nitrate	Alcohol
Disposal route	Source in lithography	Pressroom	Pressroom	Pressroom	Pressroom	Pressroom
	Collection/storage	80% to printed copy, 20% to drain	80% to printed copy, 20% to drain	80% to printed copy, 20% to drain	80% to printed copy, 20% to drain	80% evap. to air 20% to drain
	Treatment	20% to WW treatment	20% to WW treatment	20% to WW treatment	20% to WW treatment	20% to WW treatment
	Disposal/use	To surface water	To surface water	To surface water	To surface water	To surface water
Entry level	Amount	6,170 lb/yr to drain	38 gal/yr to drain	94 lb/yr to drain	—	—
	Frequency	Daily	Daily			
	Concentration	Very low	Very low			
	Distribution	Wide	Wide			
Biological impact	Movement	Water soluble [e]	Moves in P cycle	Water soluble [e]	Water soluble [e]	Water soluble vapor press. 33 torr @ 20° C [e,k]
	Partition coefficient/bio-concentration factor	—	—	—	—	—
	Stability/persistence	Biodegradable	Essential nutrient in biosystems	CrVI tends to CrIII, the less toxic form	Nitrate = nutrient Zinc=accessible	BOD = 0.16-1.68 g/g @ < 500 mg/l [a, f]
	Toxicity	Nontoxic [e]	Orl-rat LD_{50} 1630 mg/kg [g] Skn-rbt LD_{50} 2740 mg/kg [g]	Highly toxic [e] CrVI 96-hr LC_{50} Fathead = 33 mg/l [j] CrIII 96-hr LC_{50} Fathead = 27 mg/l [j]	High	Lethal 24 hrs fish 500-1000 mg/l [e]
	Ultimate sink	Returned to natural cycles	Returned to natural cycles	—	Remains accessible	Returned to natural cycles
	Environmental hazard	Low	Low	Low (based on entry level)	Low (based on entry level)	Low

Table 6. Plate coatings
(13,000 lb/yr – U.S. usage in litho)

		Diazo	Resins	Organic acids	Pigments	Indicator dyes
Disposal route	Source in lithography	On plates	On plates	On plates	On plates	On plates
	Collection/ storage	1. Plate room to WW (~1/3) 2. Pressroom to plant trash system (~2/3)	1. Plate room to WW (~1/3) 2. Pressroom to plant trash system (~ 2/3)	1. Plate room to WW (~1/3) 2. Pressroom to plant trash system (~2/3)	1. Plate room to WW (~1/3) 2. Pressroom to plant trash system (~2/3)	1. Plate room to WW (~1/3) 2. Pressroom to plant trash system (~2/3)
	Treatment	1. To WW treatment 2. None, incineration, or to plate recycle	1. To WW treatment 2. None, incineration, or to plate recycle	1. To WW treatment 2. None, incineration, or to plate recycle	1. To WW treatment 2. None, incineration, or to plate recycle	1. To WW treatment 2. None, incineration, or to plate recycle
	Disposal/use	WW to surface water, solid waste to landfill	WW to surface water, solid waste to landfill	WW to surface water, solid waste to landfill	WW to surface water, solid waste to landfill	WW to surface water, solid waste to landfill
Entry level	Amount	346 lb/yr to drain 694 lb/yr to landfill	3,240 lb/yr to drain 6,510 lb/yr to landfill (Total = 0.000003% of U.S. total prod. [q])	43 lb/yr to drain 87 lb/yr to landfill	650 lb/yr to drain 1,300 lb/yr to landfill	43 lb/yr to drain 87 lb/yr to landfill
	Frequency	Daily	Daily	Daily	Daily	Daily
	Concentration	Very low	Very low	Very low	Very low	Very low
	Distribution	Wide in water Localized in landfills	Wide in water Localized in landfills	Wide in water Localized in landfills	Wide in water Localized in landfills	Wide in water Localized in landfills
Biological impact	Movement	Water soluble	Low	Water soluble	Water insoluble [d]	-----
	Partition coefficient/bio-concentration factor	-----	Probably low	-----	-----	-----
	Stability/ persistence	Unstable to heat, light, in water Diazo group is replaced with OH. Further degradation prods. unknown.	Polymerized forms generally stable	Biodegradable	Fairly stable	-----
	Toxicity	Not well established; could be carcinogenic	Polymerized forms generally low	Low	Many are toxic	-----
	Ultimate sink	Questionable	Lithosphere	Returned to natural cycles	Variable	-----
	Environmental hazard	Low (based on entry level)	Low	Low	Low (based on entry level)	Low (based on entry Level)

Table 7. Inks
(150,000,000 lb/yr [f] – U.S. usage in litho, 1972)
(See "Reactive Solvents" for viscosity reducers.)

		Oil vehicles	Driers	Pigments (4,300,000 lb/yr to landfill [f])		
				Lead chromate	**Prussian blue**	**Organic pigments**
Disposal route	Source in lithography	Pressroom 90% to printed prod., 10% to waste	Pressroom 90% to printed prod., 10% to waste	Pressroom 90% to printed prod., 10% to waste	Pressroom 90% to printed prod., 10% to waste	Pressroom 90% to printed prod., 10% to waste
	Collection/ storage	10% waste–plant trash system (some to air)	10% waste–plant trash system	10% waste–plant trash system	10% waste–plant trash system	10% waste–plant trash system
	Treatment	None or incineration	None or incineration	None or incineration	None or incineration	None or incineration
	Disposal	Landfill or dispersed in air	Landfill or dispersed in air	Landfill or dispersed in air	Landfill or dispersed in air	Landfill or dispersed in air
Entry level	Amount	11,000,000 lb/yr to landfill [f]	500,000 lb/yr to landfill [f]	-----	-----	-----
	Frequency	Daily	Daily	Daily	Daily	Daily
	Concentration	Low in solid waste	Low in solid waste	Low in solid waste	Low in solid waste	Low in solid waste
	Distribution	Localized in landfill, widespread in air	Localized in landfill	Localized in landfill	Localized in landfill	Localized in landfill
Biological impact	Movement	Low	Oil soluble	5.8×10^{-6} g/100 cc water [c]	Insoluble [c]	Insoluble [d]
	Partition coefficient/bio-concentration factor	Not likely	Probable	Pb: B.F. = 40,000 phytoplankton 4,000 mollusk	Very low	-----
	Stability/ persistence	Probably biodegradable	Slowly biodegradable	Chemically reactive	Stable	Questionable
	Toxicity	Low	High (most contain Co, Mn, Pb)	Highly toxic [e] Scu-rat tdl 1200 mg/kg [g] Irp-gpg LD_{50} [e] 400 mg/kg [g] U.S. occ. std. air 0.1 mg/M^3 (as CrO_3)	Low in this form [e]	Some are high
	Ultimate sink	Returned to natural cycles	- Organics returned to natural cycles - Metals remain accessible	Remains accessible	Lithosphere	Returned to natural cycles
	Environmental hazard	Low	Low (based on entry level)	Low (based on entry level)	Low	Low (based on entry (level)

Table 8. Other

		Aluminum plate backing	Alcohol developers	Gum coatings	Blankets rubber/fabric	Paper	Organic liquids, solvents	
							Nonreactive	Reactive
	Source in lithography	Plate room, pressroom	Plate room	1. Plate room - to rags 2. Pressroom - to WW	Pressroom	Pressroom	Plate room, Pressroom	Pressroom
Disposal route	Collection/ storage	Most to recycle	Most to drain some evap. to air	1. To plant trash system 2. To WW treatment	To plant trash system	10% to plant trash system	To drain, to air	To air or recovered
	Treatment	Recycle	To WW treatment	None, incineration, or WW treatment	None, or incineration	None, incineration, recycle?	None, WW treatment	None, incineration, or recycle
	Disposal/use	Reused	To surface waters	Solid waste to landfill, WW to surface waters	To landfill or air	To landfill or air	1. Dispersed 2. To surface waters	Dispersed in air or recycle
	Amount	7.2 million lb/yr	220,000 gal/yr (< 0.1% of U.S. total)	563,000 lb/yr plate room rags 63,000 lb/yr washed to drain in pressroom	5,000 ft³/yr to waste	500,000 tons/ yr to waste [p]	863,000 gal/yr [o] (47% of total solvents used in litho)	978,000 gals/yr [o] (53% of total solvents used in litho)
Entry level	Frequency	Daily	Daily	Daily	Quarterly	Daily	Continuous during printing	Continuous during printing
	Concentration	Recycled	Very low	Low	0.3 ft³/ landfill/yr*	28 tons/land-fill/yr*	Low	Low (regulated)
	Distribution	Recycled	Wide in air & water	Wide in water, localized in landfill	Localized in landfills	Localized in landfills	Wide	Wide
	Movement	Low	Water soluble vapor pressure 33 torr @ 20° C	Water soluble [e]	Low	Low	High	High
Biological impact	Partition coefficient/bio-concentration factor	Low	PC = 0.05 BF= 1.41	-----	N/A**	-----	Bioconcentration possible	Bioconcentration possible
	Stability/ persistence	Stabilizes by formation of oxide (Al_2O_3) on surface [b]	BOD 0.16-1.68 g/g @ < 500 mg/l [e,f]	Biogradable	Stable	Slowly bio-degradable	Probably bio-degradable	Slowly bio-degradable, photochemically reactive
	Toxicity	Low	Lethal 24 hrs fish 500-1000 mg/l[g] appears on proposed EPA list of hazardous substances [n]	Nontoxic [e]	Low	Low	Moderate	Moderate

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*Assume 18,000 landfills in the United States.

**N/A = not applicable.

Table 8. Other (continued)

	Aluminum plate backing	Alcohol developers	Gum coatings	Blankets rubber/fabric	Paper	Organic liquids, solvents	
						Nonreactive	Reactive
Ultimate sink	Lithosphere	Returned to natural cycles	Returned to natural cycles	Lithosphere	Returned to natural cycles	Returned to natural cycles	Returned to natural cycles
Environmental hazard	Low	Low	Low	Low	Contributes to total solid waste problem, but otherwise innocuous	Low (based on entry level)	Low (based on entry level)

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Table 9. Potential environmental hazard

Low	Low, based on entry level
Resins	Reactive solvents
Organic acids	Ammonium dichromate
Gum	Zinc nitrate
Phosphoric acid	Driers
Alcohols	Diazo compounds
Aluminum	Indicator dyes
Rubber/fiber blankets	
Paper	
Nonreactive solvents	
Oil vehicles	

CONCLUSIONS

The low entry levels and biological impact of waste products from plate and press rooms make lithography an environmentally-acceptable process. Control of photochemically-reactive solvents is already recognized as important in the industry, and should be continued for good environmental stewardship. Data is incomplete on the biological impact of heavy-metal-containing components in ink driers and pigments, but their entry levels are low from the press room and can be adequately handled by conventional waste management systems.

ACKNOWLEDGMENT

I want to extend my sincere appreciation to R. B. Kincaid, 3M Printing Products Division, and my coworker, S. K. Welsh, for the extensive information contained herein on the lithographic printing industry and estimates on the levels and biological impact of waste materials.

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DISCUSSION

MR. FRANCIS M. ALPISER (Environmental Protection Agency, Philadelphia, Pennsylvania): I am a little concerned about the ultimate environmental impact of new chemicals that are developed and coming out each year. Do you see industry voluntarily trying to monitor the impact of these chemicals upon our environment and biosphere? Or do you see that not to be something done voluntarily, but which will have to be required by legislation passed by Congress?

DR. BOHON: Well, let me speak just for 3M.

In one of my jobs, I am charged with the responsibility of taking a look at every new and modified product introduced by 3M Company from the perspective of what the environmental risk will be. We do the best we can with the data that we can find or develop. We obviously cannot go into very extensive long-term chronic studies, but if it is a material that shows great promise to our company as an important material, then we want to be very certain that down the pike we are not going to get tripped up with some kind of environmental problem, so we do our best to try and assess whether or not that material will result in some kind of an undue environmental hazard.

So in answer to your question, I think that industry, at least our industry, wants to know how materials we introduce in the environment are redistributed. That is what it boils down to--redistribution of materials from one point to another: a concern that they can be safely disposed of, that the systems exist for their disposal, and that they will not cause any undue environmental hazard.

CHAIRMAN SCHAEFFER: Dr. Bohon, you were willing to speak for 3M Company at one stage. I think the question has philosophical problems if we try to speak for industry generally. So concerning the environmental impact, we are talking about several levels in terms of industry--from the prime manufacturer to the user of a chemical in processing or formulating, through an industrial user of a chemical. Now, I believe the intent here is to talk about the prime source of supply for a given chemical.

DR. BOHON: (To F. Alpiser) I am not sure whether that is what you had reference to or not: the prime source of chemical supplied (the prime manufacturer) or a formulator?

MR. ALPISER: I am concerned with the new chemicals that are introduced each year. To give you a little bit of a background, I was 25 years in the chemical industry myself, and worked for a company that produced over 2,000 chemicals. The rate of new chemicals coming out each year is just tremendous. I do not really think that in most cases the environmental risk is being assessed in the manner in which 3M describes. I am a little concerned about it, and wondered exactly how industry feels about it versus a mandated requirement, which as you probably know, has been considered.

CHAIRMAN SCHAEFFER: I think it is a question to be pondered very seriously about industry, when you have that type of broad-based problem. Dr. Bohon, do you have any more comments on that?

DR. BOHON: Only to say that I think we are willing to consider and apply whatever kind of test method can really give some vital, significant information at reasonable cost. We do not want to be forced into making a bunch of measurements that really have no relevance or significance. And so, I guess if I were to make any kind of a comment at all, it would be a plea for flexibility and the freedom to update test methodologies and so forth, as science suggests this can be done. It just does not pay to get locked into some kind of a test that subsequently you find out really has no meaning whatsoever.

MR. THEOPHILUS R. CARSON (Food and Drug Administration, Washington, D.C.): As you know, when food additives, new chemicals, are filed, we require an environmental impact analysis report. This is in order to try and keep track of just what is going on. One of the most difficult ones has been the bottle.

CHAIRMAN SCHAEFFER: Very appropriate.

MATERIALS OF FLEXOGRAPHY

K. A. Bownes*

Abstract

Flexography is possibly the most versatile of all printing processes. It is used to print almost any type of substrate. Products printed flexographically are mainly used by the packaging industry.

The inks used for flexographic printing are formulated from a wide variety of resins, solvents, pigments, plasticizers, and various additives. The ink film is required to perform under a wide variety of end-use conditions encountered during the life span of the printed product.

Flexography is a rotary typographic process using a simple ink distribution system and very fluid inks. The inks dry by evaporation of volatile solvents or, in the case of water-base inks, by absorption into the substrate. The flexible printing plates are usually molded in natural rubber. Although flexographic printing is mechanically simple, it is a very versatile printing method and can print a wider variety of substrates than almost any other process.

The differences between the flexographic printing unit and conventional letterpress ink distribution systems are shown schematically in figure 1. As many as six print stations may be found on central impression cylinder (CIC) flexo presses. Fountain covers are used to minimize solvent loss before ink transfer takes place. Even so, some is lost before entering the dryer. Modern presses are equipped with high-velocity dryers in which air literally "scrubs" the solvent from the printed surface at moderate temperatures (generally below 250° F). Air velocities are usually between 6,000 and 12,000 feet per minute while total exhaust can be in the 7,000- to 15,000-CFM range. A recent survey (ref. 1) indicated that total solvent evaporation from flexographic plants averaged about 60 pounds/hour. More accurate figures are difficult to obtain since the industry is so widely scattered throughout the country.

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*Manager, Technical Liaison, Inmont Corporation, Clifton, New Jersey.

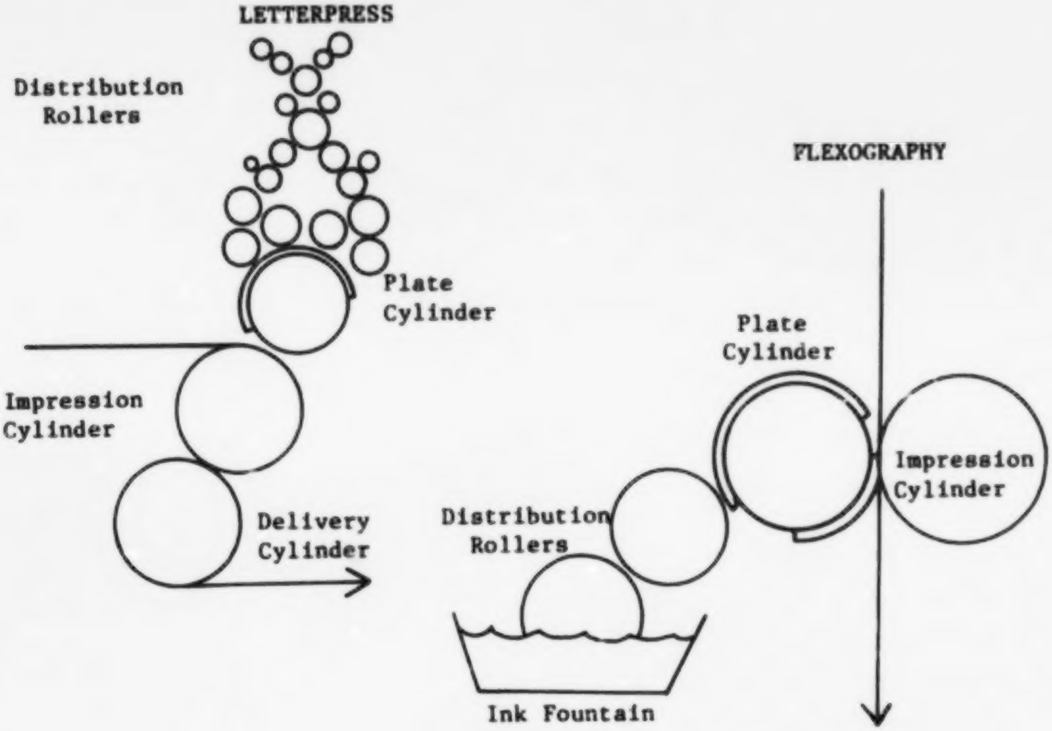
LETTERPRESS
Distribution Rollers
Plate Cylinder
Impression Cylinder
Delivery Cylinder
FLEXOGRAPHY
Plate Cylinder
Impression Cylinder
Distribution Rollers
Ink Fountain

Figure 1. Ink distribution system.

The major categories of the flexographic market are: flexible packaging and laminates, multiwall bags, milk cartons, folding cartons, corrugated paper, paper cups and plates, labels, tags tapes, envelopes, books, and gift wrap. The substrates involved in flexography are: paper and paperboard (all grades), polyethylene, aluminum foil, cellulose acetate, polystyrene, vinyl and vinylidene chloride copolymers, and laminations of the above.

It may be concluded then that flexographic inks have to do much more than be decorative. They must also have flexibility, adhesion, printability, resistance to heat, cold, sunlight, moisture, abrasion, and must possess low residual odor. To do all this requires a wide variety of ink vehicle components which function as shown in table 1.

Table 1. Typical flexographic vehicle composition

Component	Function
Resin	Adhesion, product resistance, gloss, disperses pigment
Solvent	Dissolves resin, controls viscosity, controls drying
Plasticizer	Flexibilizes resin
Lubricant	Controls rub and coefficient of friction
Defoamer	Controls foam in aqueous ink

When formulating solvent-base inks, there are a wide variety of resins to choose from to achieve the desired ink properties. The main limitation is that the resin must be soluble in a solvent that will not be too harmful to rubber. Typical resins are shown in table 2.

A much more limited choice is available when formulating aqueous inks. Amine salts of acidic resins and polymers form the vehicle system for most water-base inks. These are shown in table 3. Emulsions or "latices" lack

Table 2. Resins and typical application

Resins	Typical application
Nitrocellulose	Most solvent inks, particularly where heat resistance is required
Other cellulose derivatives	Laminating inks and special purpose plastic films
Shellac	Water-base inks, milk cartons
Ketone-aldehyde condensates	Laminations
Acrylics	Laminations, inks for vinyl and vinylidene polymers
Rosin derivatives	Inks for paper, aqueous inks
Polyamides	Polyolefins and other plastics
Phenolics	Dye inks
Urethanes	Adhesives

Table 3. Resins for aqueous inks

Resin	Types
Resin (acidic)	Shellac, modified rosins
Protein	Soya protein, casein
Polymeric	Styrene-acrylic copolymers, Ethylene-maleic copolymers
Latex	Emulsions of styrene-butadiene vinyl acetate, acrylics, etc.

the true viscosity or "tack" needed for even distribution of ink and are only used as modifiers for other resins.

In order for the resin to fulfill its role in the flexographic process, it must be applied from a suitable solvent system. Normally a combination of solvents is required to make a satisfactory ink. Many factors must be balanced, such as proper viscosity, drying speed, gloss of the dried ink film, and low retention in the print. Table 4 shows typical solvents, their evaporation rates (ref. 2) related to water = 1, and their Threshold Limit Values (ref. 3).

A convenient source for a cross section of plasticizers can be found in the Food Additives Regulations. Plasticizers for flexographic inks include: acetyl tributyl citrate, acetyl triethyl citrate, butyl phthalyl butyl glycolate, butyl stearate, dibutyl sebacate, dibutyl phthalate, diethyl phthalate, diisobutyl adipate, diisooctyl phthalate, epoxidized soybean oil, ethyl phthalyl ethyl glycolate, 2-ethylhexyl diphenyl phosphate, di-2-ethylhexyl phthalate, glyceryl triacetate, propylene glycol, and triethyl citrate. Lubricants and additives include: paraffin and microcrystalline waxes, polyethylene wax, stearamide, erucamide, silicone fluids (lubricants and defoamers), and octyl alcohol (defoamer).

Because of the vast range of colors demanded by the purchaser of packaging materials, a wide selection of colorants is needed for color matching. At the same time, the many performance requirements mentioned

Table 4. Flexographic solvents

Type	Examples	Drying rate (water-1)	Threshold Limit Value (ppm)
Alcohols	Methanol	5.75	200
	Ethanol	3.89	1,000
	Isopropanol	4.00	400
	n-Propanol	2.39	200
Esters	Ethyl acetate	10.86	400
	Isopropyl acetate	9.50	250
	n-Propyl acetate	5.78	200
Glycol Ethers	Cellosolve[a]	1.06	200
	Dowanol PM[b]	2.30	-
	Methyl Dioxitol[c]	0.06	-
Glycols	Ethylene glycol	0.03	-
	Propylene glycol	0.03	-
Miscellaneous	2-Nitropropane	3.06	25
	Hexane	24.72	500
	Water	1.00	

[a] TM, Union Carbide Corp. Mono ethyl ether of ethylene glycol.

[b] TM, Dow Chemical Co. Mono methyl ether of propylene glycol.

[c] TM, Shell Chemical Corp. Mono methyl ether of diethylene glycol.

earlier, such as resistance to bleed in wax or plasticized films, must still be met.

The first group of colorants includes white, black, and the inorganics. These are: titanium dioxide; calcium carbonate; clay (kaolin); aluminum powders; carbon black (furnace and channel process); iron oxides (yellow, red, black); lead chromate yellow; molybdated lead chromate orange; and iron blue (ferric ferrocyanide).

Many organic colors are azo couplings. This category accounts for most yellows, oranges, and reds. Table 5 shows the most important of these with typical color index numbers (ref. 4).

Table 6 shows blues, violets, and greens. For resistance properties, the phthalocyanine derivatives are most important. Methyl violet, Victoria

Table 5. Azo couplings with their typical color Index numbers (ref. 4)

Pigment	Color index no.
Hansa yellow	11730
Diarylide Yellow	21095
Dianisidine orange	21160
Diarylide orange	21110
Naphthol red	12315
2B red	15865
Lithols (Ba,Ca,Sr,Na)	15630
BON red	15860
Red lake C	15585
Lithol rubine	15850

Table 6. Blue, violet, and green pigments

Pigments	Color index no.
Phthalocyanine blue	74160
Phthalocyanine green	74260
Alkali blue	42750A
Victoria blue	42595
Methyl violet	42535
Malachite green	42000

blue, alkali blue, and malachite green are triphenyl methane derivatives used as phosphotungstic or phosphomolybdic acid lakes. Other miscellaneous colors include rhodamines, dioxazines, and quinacridones.

Flexo inks containing soluble dyes make up a smaller segment of the market for such applications as envelopes, paper tapes, some glassine wrappers, and background tints on paper. Basic dyestuff is mainly used, usually laked with phenolic resin. Typical dyes are shown in table 7.

Table 7. Dyes for flexo inks

Dye	Color index no.
Auramine	41000
Rhodamine	45170
Methyl violet	42535
Victoria blue	44045
Brilliant green	42040

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3. NPIRI Raw Materials Data Handbook, Vol. 1, NAPIM Technical Institute at Lehigh University, Bethlehem, Pa., 1974, pp. 12-25.
4. Colour Index, Third Edition (1971), The Society of Dyers and Colourists (England) and The American Association of Textile Chemists and Colorists, Research Triangle Park, North Carolina.

DISCUSSION

MR. THEOPHILUS R. CARSON (Food and Drug Administration, Washington, D.C.): How do you dispose of your resins?

MR. BOWNES: Are you referring to waste ink?

MR. CARSON: Right.

MR. BOWNES: That is normally taken away by a contractor and disposed of in a sanitary landfill. Some inks are incinerated. But then of course the sludge, the residue, the pigment, which do not incinerate, and whatever is left of the resin, go to a sanitary landfill eventually.

ENVIRONMENTAL IMPACTS OF CHEMICALS USED IN SCREEN PRINTING INKS

Charles F. Call, Jr.*

Abstract

Screen printing is the most versatile of all printing processes because of its ability to print on any substrate. Next to gravure, screen printing uses the highest solvent-content inks. This high solvent content, coupled with the wide range of solvents that must be used to formulate inks for diverse substrates, constitutes the primary environmental impact of materials used in screen printing inks.

SCOPE

This paper will explore the raw materials used in screen printing inks, especially solvents, that have the greatest environmental impact. The author will consider possible environmental impacts from the printer's viewpoint. Although many different chemicals will be discussed, it is not within the scope of this paper nor within the author's expertise to explore their specific impact or deterimental effects.

Because of screen printing's diverse uses, the industry has divided itself into many groups, all falling under the auspices of the Screen Printing Association. For the purpose of this paper, the author has divided screen printing into only two groups: electronics and commercial. The electronics group covers the use of screen printing for printed circuit boards. The commercial group covers decorating, display, advertising, textiles, and other factions of screen printing not connected with electronics. The division was made because of the end use of the ink film and the possible environmental impacts of that use.

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*Technical Service Applications Engineer, Wornow Products Department, Hysol Division of Dexter Corporation, Olean, New York.

INTRODUCTION

Screen printing is the most versatile of all printing processes. Its ability to print on any substrate has given impetus to rapid growth over the past few years. In conjunction with diverse substrate advantages, ink deposit and color strength have created markets for screen printing in areas including printed circuit boards, display advertising, textiles, and decorating.

These advantages of screen printing have promoted the formulation of many different inks to meet substrate and end-use requirements. The raw materials used for these inks are chosen by their ability to perform in relation to the particular substrate and end use. Solvents, our primary concern, are chosen for their ability to work with the proper raw materials and for their substrate advantages, as well as their fitting the needs of the screen printing process.

Much of the information in this paper is based on courses taken by the author during undergraduate studies in the College of Graphic Arts and Photography, Rochester Institute of Technology, Rochester, New York. Additional information was garnered from James Hornburg and Jerry Lutz, Hysol Division, The Dexter Corporation, and the author's personal experience.

THE SCREEN PRINTING PROCESS

Screen printing is a stencil process. Stencils are made mechanically or photographically and mounted on precision-woven fabric for support. Ink is printed through the stencil and fabric by a "squeegee" and deposited on the substrate. This transfer from screen (combination of stencil, fabric, and a frame to hold the fabric) to substrate is accomplished by hydraulic pressure, applied by the squeegee, to ink present in the "holes" of the fabric, and also by the affinity of the ink for the substrate--over the fabric and stencil.

This type of printing requires a fluid ink. Screen printing inks are usually 50 to 80 percent solid materials; that is, pigment, resin, and filler make up 50 to 80 percent of the mass, while solvent contributes the rest of the formulation. Only gravure (and flexography) can claim a higher solvent content.

Substrates vary greatly. Many shops specialize in certain types of screen printing and the substrate they print reflects their specialization. Poster shops work with paper. Decal shops work with decal paper and recently with pressure-sensitive synthetics. Metal decorating shops frequently use screen printing on aluminum, steel, and other metals. Circuit shops print on copper laminated on epoxy fiberglass boards. Because of different end-use requirements, substrates cause special ink selections. Quality requirements for the end use of the printed piece do not allow for universal inks.

SCREEN PRINTING INK FORMULATION

Screen printing inks are virtually all "conventional-curing." That is, the inks cure in either room temperature air or in a heat-generating oven. Inks are formulated with three primary areas in mind: substrate, end use, and screenability. Secondary areas of concern include cost, raw material availability, production feasibility, and competition.

Conventional inks contain resins, fillers, and solvent. "Resin" is a broad-based term for the raw material that is the film former of an ink. Resins are chosen for their substrate and end-use advantages. Typical resins are alkyds, resin esters, epoxies, and vinyls. The compatibility of a resin with solvents and fillers generally used in screen printing is also considered.

Fillers are usually inert materials used to bring the formulation to a screenable thickness or color. Fillers may also to some extent improve opacity and adhesion to substrates. Typical fillers used are clay, calcium carbonate, some silicates, and pigments.

When combined with resins, solvents constitute the "vehicle." Solvents, for screen printing, are chosen by their solvent power, flash point, boiling range, and toxicity. Solvent power is the ability of a solvent to dissolve a particular resin. While some solvents are excellent for dissolving vinyls, this same solvent will not touch an alkyd resin.

The flash point is simply the solvent's ignition point, or more precisely the mean temperature at which solvent vapor escaping from a liquid will form a combustible mixture with air and ignite when exposed to an open flame (ref. 1).

The boiling range of a solvent is the temperature at which its vapor pressure equals atmospheric pressure. Simply put, the higher the boiling range, the slower the solvent evaporates. Solvents for screen printing generally have boiling ranges in excess of 340° F (ref. 1).

Toxicity is a concern because solvents have multiple accesses into the human body. Solvents may be taken in through inhalations of solvent vapor, absorption through the skin, or ingestion through the mouth. Certain solvents produce dermatitis, or inflammation of the skin; some can produce narcosis, or unconsciousness, and some can affect the kidney, brain, or other vital organs. Of course, a very high concentration of any solvent vapor could have serious physiological effects just by depriving oxygen sufficient for normal activities. Toxicity can generally be prevented by following handling instructions and, above all by providing adequate ventilation (ref. 1).

Three solvent types are commonly used in screen printing inks. They are aliphatic hydrocarbons, aromatic hydrocarbons, and oxygenated solvents. Of the three types, only oxygenated solvents generally fall under what is known as "exempt solvent" classifications. Exempt solvents came into existence through Los Angeles "Rule 66", a stiff antipollution act; they exhibit lower levels of the hydrocarbon emissions that form photochemical smog.

While both the aromatic and aliphatic hydrocarbon solvents exhibit the properties needed for manufacturing screen printing inks, the trend in formulation has been towards exempt oxygenated solvents. This trend has developed because of the concern of screen printers and suppliers for complying with Federal and local antipollution regulations.

Oxygenated solvents can be chosen from esters, ethers, glycol ethers, and ketones.

In addition to the three main ingredients in screen printing inks, additives such as plasticizers, flow agents, and antiscum agents are used to improve the printability and film properties of the ink.

POLLUTION CONCERNS

Screen printing inks normally cure, at least partially, by solvent evaporation. Secondary curing is by thermosetting, oxidation, polymerization, or penetration. Printed circuit board resists or inks generally do not cure at all, but merely "set up" through solvent evaporation.

Screen printing's major contribution to pollution is through solvent evaporation. However, very few shops produce large enough volumes of evaporated solvent to cause any significant menace. All shops have alternatives. The use of exempt solvent inks is one. Low solvent content, using exempt solvents, also helps. Some segments of the industry can use water-base inks; others can use ultraviolet cured, 100 percent solids materials. Alternate curing methods are being developed.

In short, the screen printing industry is well within current anti-pollution guidelines, on paper. There are still shops using nonexempt solvent materials and they are polluting. However, as tougher State and local regulations come into existence, these shops will have to comply, and the means to comply are close at hand.

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ENVIRONMENTAL IMPACT OF CHEMICALS USED

William D. Schaeffer, Ph.D.
Chairman

GRAVURE INDUSTRY'S ENVIRONMENTAL PROGRAM

Harvey F. George*

Abstract

Gravure is one of the three major printing processes. It differs from letterpress and offset lithography in that the recessed or intaglio image of gravure permits the use of a very fluid ink that can be dried with low-temperature forced-air driers between printing stations. The solvent-laden air from the driers ideally can be directed through an activated carbon bed where the solvent is adsorbed and recovered. This paper presents an overview of the gravure printing process and industry, reviews the environmental regulations applicable to gravure, and discusses the gravure industry's environmental program set up by Gravure Research Institute and Gravure Technical Association to assist gravure printers and engravers in complying with these regulations.

Nature of the Gravure Printing Process

Gravure is one of the three major printing processes that may be characterized by the nature of their image formations. The gravure image is a recessed or intaglio image, as compared to the relief or raised image of letterpress and the planographic or surface image of lithography. The gravure-image carrier is a copper-plated cylinder or copper plate, and the image is in the form of cells or cups engraved in the surface. Typically, a gravure cell is 35 μ (.0014 in.) deep by 125 μ (.005 in.) square, with 22,500 cells to the square in. (150-line screen). The walls between cells are known as the bridge or doctor blade support, and the intersections between the walls are called the corner posts. The gravure cylinder is flooded with a liquid gravure ink. The excess ink is doctored off with a .006- to .010-in.-thick Swedish blue steel doctor blade. The ink is then transferred to the paper to be printed by pressing the paper against the cylinder as it turns,

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*Executive Vice President and Research Director, Gravure Research Institute, Inc., Port Washington, New York.

using a rubber-covered impression roll of 70- to 85-shore A durometer hardness (ref. 1).

Uses for Gravure Printing and Coating

Gravure printing and coating applications fall into three major categories, i.e., publication, packaging, and specialties. In the publication field, magazines, mail order catalogs, brochures, newspaper supplements, comics, and other types of commercial printing are printed by the gravure process. Folding cartons and flexible packages, including such items as soap cartons, ice cream cartons, flip top cigarette packages, frozen food wraps, composite foil cans, 1-1/4-mm polyethylene bread bags, etc., are typical gravure printed packaging products.

In the specialty field, gravure is used for producing wall and floor coverings, decorated household paper products such as towels and tissue, cigarette filter tips, vinyl upholstery, wood grains, and a wide variety of other products. Gravure is also used for applying accurately metered quantities of coatings to paper and other kinds of webs in various manufacturing operations where the fast-drying inks used in gravure and the ability to print well on a wide variety of surfaces are advantageous.

Nature of the Gravure Printing Industry

Gravure-printed products are roughly 31 percent in the specialty field, 26 percent in packaging, and 43 percent in publication (ref. 2). The estimated volume of gravure printing in all categories was about $4 billion in 1974 (ref. 3).

Publication printing is done by a relatively small number of companies with large printing plants, numbering less than 50 in total. Package and specialty printing by gravure is done by a considerably larger number of companies, ranging from large integrated packaging companies with many gravure press units to small captive operations with only one or two press units. It is estimated that there are from 13 to 14 thousand gravure printing units in the United States (ref. 4).

A printing unit consists of a gravure cylinder and an impression roll, with associated inking and doctoring mechanisms. A gravure press may consist of from 1 to 8 or more units that are coupled together with associated paper feeding and roll-or-folder-delivery arrangements. One or more gravure units may run as an in-line operation coupled together with other printing, coating, or converting operations.

The gravure industry is served by two industry-supported organizations: the Gravure Technical Association, a trade association, which is concerned with customer and trade relations, standardization, and education; and the Gravure Research Institute, a not-for-profit cooperative research organization, which is concerned with research on gravure printing and related operations, and with materials such as paper and ink.

Preparation of the Gravure Printing Surface

Preparation of the gravure printing surface starts with copper plating the gravure cylinder, which may range in size from a cylinder only 3 in. in diameter and 1 in. wide for printing on pharmaceuticals, to a cylinder 17 or 18 ft long and 3 or more ft in diameter, for printing on linoleum. Publication and larger packaging or coating cylinders are usually integral-shaft steel bases that are centrifugally cast with a .060-in.-thick deposit of cyanide bath copper, followed by a .006-in.-thick strippable layer of copper from an acid copper sulfate bath. After plating, the copper surface is polished to a 6- to 10-μin.-finish and to close dimensional tolerances on diameter, e.g., ±.001 in. diameter and .001 in. TIR concentricity. Smaller cylinders for packaging or specialty printing may have integral shafts or may be of the sleeve type, using a mandrel or cone and a removable shaft. Cylinder base material may be steel or aluminum tubing. Copy to be engraved on the gravure cylinder must be converted to photographic positives typically made to a density range from 0.35 to 1.65 density units. The photographic steps of color separation, color correction masking, etc., are common to all printing processes and need not be discussed separately for gravure.

Either of two methods is used to screen the gravure images in order to form the gravure cells or cups: 1) a cross-line screen with clear lines and opaque dots is used to expose the resist together with the continuous positive (conventional gravure); or (2) a half-tone positive with variable dot size is made from the continuous-tone positive with a density range from .05 to .30 integrated density units (lateral hard-dot gravure). The continuous-tone positive controls the cell depth, while the screen or half-tone positive determines the cell area. Consequently, conventional gravure has constant area variable depth cells, while half-tone gravure has cells that vary both in area and depth.

Etching resists may be either of the diffusion type or stencil type. Publication printing and process color printing for packaging and specialty items is most often done with a diffusion resist, which may be either a potassium bichromate, light-sensitized, pigmented, gelatin-coated paper called carbon tissue, or a silver halide gravure-resist photographic film. The diffusion resist is exposed with a high-intensity light source in register to the continuous-tone positive and half-tone positive, in succession. The resist is hardened or made water-insoluble in proportion to the amount of light passing through the positive. After exposure, the resist is transferred to a "water-wettable," clean, polished, copper, gravure cylinder by wetting the surface and rolling the resist face down in contact with the copper. For publication work, the resist is in page size sheets, while for packaging or coating cylinders, a single large sheet of resist may be used. After transfer of the resist to the cylinder, the cylinder is soaked in hot water for approximately 15 to 20 min. This is done to remove the backing paper and to dissolve away the unhardened gelatin. A variable-thickness gelatin resist thus remains over the entire surface of the cylinder, with the resist thickest in the nonprinting and highlight areas and thinnest in the shadow areas. After drying and staging with asphaltum varnish (to protect the cylinder ends and other areas of bare metal), the image is etched into the copper surface in a ferric chloride etching bath of approximately 40° Bé specific gravity that diffuses through the gelatin resist and penetrates first the thinnest areas or shadows, and finally the lightest areas or highlights. Single- or multiple-bath etches of varying Baumés may be used to obtain the desired range of cell depths. After etching, the resist is removed and the cylinder may be chrome plated for longer wear-life if desired.

With the stencil resist process, the gravure cylinder is coated with a light-sensitive photopolymer such as KPR (Kodak Process Resist), or a bichromated colloid such as gum arabic or PVA. The sensitized cylinder is exposed to a half-tone positive only, and after development may be etched with a single bath of ferric chloride. Engraving with a stencil-type resist process, which is also known as Direct Transfer Engraving, produces an essentially constant cell depth. Tonal variation results are obtained mainly from differences in cell diameters, and as a consequence, a limited tonal range is achieved. However, for line work and coating cylinders where uniform cell volume is required, a Direct Transfer process with a stencil resist is economically advantageous.

Michael (ref. 5) lists 15 processes where water contacts metals in the plating and engraving of gravure cylinders as outlined above and waste treatment is required. These 15 processes are grinding and polishing, film processing, etching, alkaline cleaning, acid pickling, copper cyanide plating, boiler water chromate processing, chromium stripping, chromium strip heating and cooling (coils), acid copper sulfate plating, carbon tissue sensitizing, chromium plating, chrome plating heating and cooling (coils), and chromium exhausting. Among the processes involved in treating waste from these processes are mechanical separation of effluent, silver recovery, cyanide oxidation and destruction, reduction of hexavalent chromium to trivalent chromium, neutralization, and precipitation. Batch treatment systems, as opposed to continuous systems, have been found to be economically practical in small- to medium-size plants, according to Michael. The safe disposal of solid waste from such treatment systems must also be considered.

Lubell (ref. 6) describes the waste water treatment system for the Newspoint Rotogravure plant of the New York News, where the total maximum average daily (design) waste water treatment has been calculated at 8,700 gallons, of which 8,000 gallons require neutralization and precipitation while the remaining 700 gallons require dilution before discharging to the city sewer.

Gravure cylinders may also be imaged by electromechanical engraving on an electronic scanner-engraving machine such as the Hell Helio-Klischograph. In this process, the copy is mounted on a scanning drum and signals from a photoelectric pickup are used to control an electromechanically driven diamond stilus that cuts pyramidal-shaped gravure cells into the surface of the gravure cylinder at the rate of 4,000 cells a second. Electronic gravure cylinder engraving machines, which were first introduced about 1958, are becoming more widespread in use and have found application in publication printing, package printing, and in specialty printing for wood grains and other seamless patterns for decorative laminates. Coating cylinders using the gravure ink transfer method may also be made by mechanical knurling. These cylinder engraving methods, while in themselves involving no water pollution problems, still require treatment for the plating and other operations.

The Gravure Printing or Coating Operation

Installation of the engraved gravure cylinder in the gravure press unit and adjustment of doctor blade, impression pressure, web-guiding rolls, unwind tension, folder, etc., constitutes the "makeready" of a gravure press.

Once the various press settings are made and the proper ink viscosity and drying conditions are achieved for proper ink transfer and printed film characteristics, the gravure printing or coating operation is relatively simple to control. Maintenance of ink viscosity is the major requirement. This is achieved by the addition of a solvent to the ink, in order to make up for evaporation. The makeup solvent should be blended to maintain the primary solvent resin mixture in the original ink formulation. The gravure cylinder, if chrome plated, can run for millions of impressions.

Gravure Printing and Coating Equipment

The basic gravure printing or coating unit consists of the engraved gravure cylinder at the bottom, with a rubber-covered impression roll at the top. The gravure cylinder is geared to, and driven by, a motor-driven shaft which drives the other gravure units or converting units in the line. The impression roll is friction-driven through the web by the gravure cylinder. For wide presses, such as are used in publication printing, the impression roll may be backed up by a steel backup roll to minimize bending. Mechanical impression screws or hydraulic or pneumatically operated impression pistons apply impression pressure to the end journals of the impression roll or back-up roll, pressing the rubber against the gravure cylinder with a pressure of 50 to 250 lb/linear in.

The gravure cylinder runs in an ink fountain or trough. In addition, spray nozzles may also be used to apply ink at a point close to the exit side of the nip. The ink fountain on high-speed presses using volatile inks is totally enclosed, except for a small area between the doctor blade and the nip and on the exit side of the nip. Enclosure of the ink fountain minimizes solvent evaporation and permits the use of fast-drying solvents which are required in high-speed printing operations.

A doctor blade holder is provided, together with an oscillating mechanism that permits adjustment of the doctor blade angle, as well as the horizontal and vertical positions of the doctor blade. Gravure press speeds range from approximately 500 to 1,000 ft/min in packaging and specialty printing, from 1,200 to 1,800 ft/min in magazine and supplement publication printing, and up to 3,000 ft/min or more in some printing operations running in line with paper machines.

Inks and Coatings for Gravure

A typical gravure ink consists of pigment, binder, and solvent in the following approximate proportions: 10, 50, 40. Pigment provides color to the ink and may consist of such materials as clay, titanium dioxide, carbon black, lithol red, red lake C, lithol rubines, chrome yellows, cadmium yellows, diarylide yellows, iron blue, phthalocyanine blue, as well as many other compounds including metallics and flourescents. Chrome yellows are being phased out because of their lead content and cadmium yellows are generally used only in some specialty products like decorative laminates because of their extreme light-fastness. Toxicity concerns in gravure inks are discussed in greater detail by Surgeon (ref. 7), Bassemir (ref. 8) and Zak (ref. 9). The basic requirement of a gravure ink is that it be free flowing. This is necessary so that it can be pumped through the ink lines to the ink fountain, in order to readily enter and leave the etched cells of the gravure cylinder, and be wiped cleanly under the doctor blade. Gravure inks must transfer readily to the paper or film, without mottle, and have adequate opacity or transparency and coverage. The ink must dry completely on the substrate under normal press operating conditions, but must not dry in the cells of the gravure cylinder. The dried print must fulfill the specific requirements determined by the nature of the printed product, whether it be a magazine, a food package, a gift wrap, etc.

The binder is the solid component of the gravure ink vehicle. It serves to lock the pigment to the substrate, as well as to protect the pigment from heat, moisture, and abrasion. Resins of various types, both natural and synthetic, are generally used as binders. In brown or black inks, gilsonite serves both as a binder and coloring agent. Zinc calcium resinates are generally used as binders for low-cost, high-speed publication inks, using inexpensive aliphatic hydrocarbon solvents. Ink for packaging, specialty printing, and coating may be formulated from a wide variety of resins including nitrocellulose, ethylcellulose, polyamides, chlorinated rubbers, and water emulsions or latices.

The solvent, which together with the binder makes up the ink vehicle, is chosen for its ability to dissolve the binder and to provide the fluid properties necessary for good inking, doctoring, ink transfer, and drying. The solvent must dry rapidly by evaporation, leaving a dry pigment binder film on the surface of the paper. Typical gravure solvents include alcohols, aliphatic naphthas, aromatic hydrocarbons, esters, glycol-ethers, ketones, nitroparaffins, and water.

Forced air dryers operating at low temperature (100° to 250° F) between the printing units of the gravure printing press are used to dry the ink. The solvent-laden air ideally can be directed through an activated carbon bed where the solvent is adsorbed and recovered for further use. This is the avenue for control of air pollution that is favored for publication gravure presses. A large system has been in operation at Triangle Publications, Inc., in Philadelphia for more than 25 years and in recent years has been expanded to recover over 10,000,000 pounds of solvent annually (ref. 10). While a number of publication gravure plants continue to operate temporarily by reformulating inks with Rule 66-type exempt solvents, a considerable number of solvent recovery systems have been installed in the last few years and others are being installed or are planned for installation in the near future (ref. 11). All new publication gravure plants are being designed to include solvent recovery, which is ecologically sound, and with increased hydrocarbon costs, economically justifiable.

In contrast to publication gravure where the same ink-solvent formulation is used routinely day after day, the packaging and specialty gravure printer must contend with a wide range of solvents depending on the substrate to be printed. Fume incineration may be required to dispose of solvent emissions in this case, as discussed by Rappolt (ref. 12). Packaging and specialty gravure printers are proceeding with programs to attain compliance with emission regulations, but the technological, economic, and energy problems being encountered are considerable, as indicated by Sallee (ref. 13).

Some of the smaller gravure printers, although willing, may have neither the technical expertise nor the economic resources to come into compliance within the scheduled deadlines. The gravure industry's environmental program was set up in recognition of their possible need for assistance.

GRAVURE INDUSTRY'S ENVIRONMENTAL PROGRAM

In response to the challenges presented to the gravure industry by the Clean Air Amendments Act of 1970, the Federal Water Pollution Control Act of 1972, and the OSHA Act of 1970, a joint gravure environmental control and occupational safety program was set up in an agreement entered into on July 12, 1972, by the Gravure Technical Association and the Gravure Research Institute. The agreement recognized the two very different characteristics of GTA and GRI and capitalized on the strength of each organization. The program had as its objective initially the accomplishment of six goals (ref. 14).

1. Gravure Environmental and OSHA Newsletter

First we wanted to set up an information clearinghouse and library for all the relevant environmental information, publications, data from the government, and other sources that might be of concern to gravure printers and engravers. Among the many references and periodicals now available in the Gravure Environmental OSHA Library, established at the GRI laboratories in Port Washington, L. I., New York, are the Federal Register and publications from EPA, both Federal and State; NIOSH; OSHA; ACGIH; AIHA; ASTM; ANSI; NFPA; HEW; ECB; BNA; CCH; NSF; and others. These publications are reviewed continuously by a full-time librarian and the GRI technical staff for developments of concern to the gravure industry. The output of this effort is the

Gravure Environmental and OSHA Newsletter, which serves as the communications link between the information clearinghouse and the members of GTA and GRI within the gravure industry. To date, six issues of the Gravure Environmental and OSHA Newsletter, totaling 430 pages, have been published and the Newsletter is serving a very useful purpose. Some examples of the variety of subject matter covered in the Newsletter are hearing conservation, noise control on the gravure press, electrical equipment in hazardous locations, solvent storage in the gravure pressroom, etc.

2. Gravure Environmental Control and OSHA Seminars

Our second goal was to organize and conduct seminars and meetings on environmental and safety matters. Four well-attended seminars and a Materials Shortage Roundtable have been held to date. Speakers from EPA, OSHA, NIOSH, and the gravure industry itself and its suppliers have contributed to the success of these meetings. The full proceedings of each meeting have been published in the Newsletter together with other articles relating to important developments in the environmental and worker safety and health fields.

3. Environmental Laboratory and Technical Service Program

Our third goal was to set up a gravure environmental laboratory at Gravure Research Institute with the instrumentation needed for the environmental control and worker safety-related measurements required in current and anticipated future legislation. Included in the environmental laboratory equipment are a Perkin-Elmer model 900 gas chromatograph, Model 307 atomic absorption spectrophotometer, sampling tube instruments, explosimeter, various personal monitoring pumps for hazardous conditions, stack emission sampling apparatus, audiodosimeters, an octave band analyzer, noise measuring instruments and various other instruments. Using this unique laboratory facility, a technical service program for the gravure industry has been established and is functioning in the following areas described by Shah (ref. 15).

a. Occupational exposure to hazardous materials such as organic solvents and metallic air contaminants.

b. Air pollution studies of solvent vapor emissions from gravure press stacks and from other plant areas.

c. Waste water analysis for metallic pollution, organic solvents, and other pollution.

d. Noise level measurements and audiodosimeter surveys of worker exposure to noise.

Among the technical services that have been performed are measurement of hydrocarbon emissions from packaging and publication gravure plants to provide data required for installation of solvent recovery systems, personnel monitoring for exposure to chromic acid in gravure plating operations, personnel monitoring for exposure to toluene and other solvents, personnel monitoring for exposure to noise, consultation on air pollution regulations, solvent storage, electrical equipment in hazardous locations, and a wide range of other environmental and OSHA questions.

4. Environmental Research and Development

Our fourth goal was for GRI to conduct research and development directed toward finding solutions to environmental and safety problems faced by gravure printers. Development of an organic solvent emission sampling and analysis procedure for gravure, as described by Shah and George, is an example of this activity (ref. 16). While GRI is not in a position to evaluate health effects of various toxic substances used in gravure, it is encouraging medical studies done by gravure printers here and abroad in these areas, such as that reported by Kunz on the influence of toluene on the health of rotogravure workers (ref. 17). Development of water-base inks is another active research area.

5. Spokesman for Industry

A fifth and most important goal of the program is to act as a spokesman for the gravure industry on environmental and OSHA matters. In this connection GRI and GTA representatives have participated in regulatory hearings in various areas and both organizations have actively supported the work of the Environmental Conservation Board of the Graphic Communications Industry, which was organized to represent the entire printing and graphic arts industry in such matters and has responded in a number of vital areas, such as toluene exposure criteria, proposed noise regulations, and others.

6. Joint Steering Committee

The sixth and final goal of the agreement was to establish a joint steering committee to guide the five activities mentioned previously. We were fortunate to have an outstanding individual, a chairman of this committee, Donald C. Cieber, of The Denver Post, Inc., who encouraged and guided the program from its inception. Mr. Cieber is now President of Gravure Research Institute.

In conclusion, I think you can well agree that the gravure industry has a substantial commitment toward providing a safe and healthy workplace for its employees and to controlling the byproducts from its operations to avoid environmental contamination.

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DISCUSSION

MR. E. J. HEISER (Dow Chemical, U.S.A., Midland, Michigan): What is the status on the water-base inks?

MR. GEORGE: Water-base inks are in regular production use in some packaging and specialty applications, such as sugar bags, for example. However, for long-run publication-type work, water-base inks have not yet been developed to the point where they are as suitable as the hydrocarbon-type inks in terms of their usefulness, their ability to run at high production speed and to give the desired film properties, and their cost. However, this is a very active research area. And it has the obvious potential of eliminating a big source of air pollution.

MR. W. N. FINGLAND (International Paper Company, Clinton, Iowa): You mentioned, very briefly, wastewater analysis by GRI. Are you doing this for members?

MR. GEORGE: Yes, we are.

MR. FINGLAND: I would like to learn more about that. Can you comment some more on it.

MR. GEORGE: We have the equipment and the capability to do wastewater analysis for our members, particularly for heavy metal contamination. This is done on a technical service basis. I will certainly be glad to talk to you about it in further detail.

STORAGE AND HANDLING OF FLAMMABLE AND TOXIC CHEMICALS

Josef F. Heller*

Abstract

With the 1975 Fire Prevention Week (October 5-11) nearly upon us, we felt this subject would be appropriate for most of our plants, but also at home. The National Fire Protection Association defines a flammable liquid as any liquid having a flash point below 140° F and a vapor pressure not exceeding 100° F. On the other hand, combustible liquids have flash points between 140° F and 200° F. These liquids vaporize and form flammable mixtures when in open containers, when heated, or when leaks or spills occur. The vapors are what burn if ignited; therefore, closed containers (safety cans) should be used when storing small quantities of the materials, and should have adequate ventilation and grounding.

Many flammable liquids and their vapors can create health hazards from surface contact and inhalation of toxic vapors. These vapors are heavier than air, and therefore seek the lowest levels possible--for instance, tanks. Tanks should always be checked for combustible and toxic vapors prior to entry. Adequate measures must be taken to reduce exposures.

The following 10 questions provide a checklist for the storage and handling of combustible or flammable mixtures: 1) Are control valves identified by color, tag, or both on all equipment containing flammable liquids? 2) Are safety cans labelled of contents and do they include flame arrestors? 3) Are dispensing drums equipped with a bung vent, spring-loaded safety faucet, and drip cans with flame arrestor screens? 4) Are containers and equipment grounded and bonded? 5) Are downspouts long enough to reach tank bottom used when loading and unloading operations? 6) Are Hazardous Work Permits used for tank entry, welding, and forklift entry? 7) Is floor clean of drips, spills, and trash? 8) Is grounding integrity OK to earth ground? 9) Are oily waster or solvent-soaked rags stored in a self-enclosing metal container? 10) Are explosion-proof

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*Safety and Security Engineer, Safety Division, Borden Chemical, Division of Borden Inc., Columbus, Ohio 43215.

electric switches and equipment in good condition?

Should any of the items in the checklist above occur in your plant, please advise your immediate supervisor. To protect your home, plant, and job, let us continue to perform our jobs in a safe manner. You have a lot at stake to protect--your job...your life.

Introduction

In just a few weeks, we will be contributing our ideas and concerns to the 1975 National Fire Prevention Week, October 5-11. For this reason, I feel my topic should lend some interest to the seminar and hopefully provide some safeguard measures you can take back to your work environments, whether it be printing ink manufacturing or the printing industry.

It is probably appropriate to first give you a few definitions. The National Fire Protection Association defines a flammable liquid as any liquid having a flash point* below 140° F and a vapor pressure not exceeding 40 psia at 100° F. Flammable liquids are usually subdivided into classes. Combustible liquids are those with flash points in the range of 140° F to 200° F. Although they do not ignite as easily as flammable liquids, they can ignite under certain conditions or circumstances, and so must be handled with caution.

Flammable liquids vaporize and form flammable mixtures when in open containers, when leaks or spills occur, or when heated. The degree of danger is determined largely by the flash point of the liquid, the concentration of vapors in the air, and the possibility of a source of ignition at or above a temperature sufficient to cause the mixture to burst into flames.

It is not the liquids themselves that burn or explode, but rather the vapor/air mixture formed when they evaporate. Therefore, handling and storing these liquids in closed containers and avoiding exposure of low-flash liquids in use are of fundamental importance.

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*A flash point of a liquid is the lowest temperature at which it gives off enough vapor to form flammable mixtures with the air and to produce a flame when a source of ignition is brought close.

The extremes of vapor or gas concentration with air which, if ignited, will just propagate flame, are known as the "lower" and "upper" flammable limits and are commonly expressed in terms of percentages in the lower or upper explosive limits (LEL or UEL). I doubt that any one of you here today has a plant atmosphere entirely free of fire and explosion hazards involving flammable liquids.

Earlier I spoke of classifications of flammable liquids and these are as follows:

- Class I - Liquids with flash points below 100° F:
  - Class 1A - Flash point below 73° F and having a boiling point below 100° F (i.e., rotogravure and solvent flexographic inks).
  - Class 1B - Flash point below 73° F and having a boiling point above 100° F.
  - Class 1C - Flash point at or above 73° F and below 100° F.
- Class II - Liquids with flash points at or above 100° F and below 140° F (i.e., make-ready inks or specialized inks).
- Class III - Combustible liquids with flash point above 140° F and below 200° F (i.e., a few offset inks).

General Safety Measures in Storage and Handling

Accidental mixture of flammable liquids should be prevented, for it may, upon later use, release vapors of its lower flash point and act as a fuse to ignite the higher flash point material.

Control valves on equipment containing flammable liquids should be identified by color, tag, or both. Color coded piping, as directed by Federal or State OSHA agencies, indicating direction of flow is most important so as not to cause confusion or a serious incident. Manifold lines from tanks of different products should not be used; separate pumps for different products should be provided.

Portable containers of Class I and II liquids should be provided in the form of approved safety cans with flame arrestors in the vent or opening. Safety cans should also be provided, with yellow bands and identification lettering placed on them so as to reserve certain containers for their respective liquids and to help reduce the chance of liquids being mixed. Drums dispensing flammables should also be equipped with flame arrestor bung vents and spring-loaded safety faucets and drip cans.

Flammable liquid drum storage, both indoor and outdoor, presents a serious fire and explosion hazard. It is crucial to provide safe storage facilities. The safest practice is to store flammable liquids in buried tanks out of doors and to pump the liquid through a closed piping system to the point of use with an approved pump equipped with an automatic flow control to stop liquid flow in case of emergency. In the case of aboveground tanks, diking would be necessary. This is standard recommended practice where liquids are delivered by tank truck or tank car. Flammable liquids in unopened containers offer a moderate hazard, but when metal drums are exposed to fire, they become dangerous and could burst with explosive violence. Fifteen percent of all industrial fires and explosions involve the storage and handling of flammable liquids.

Indoor storage should include:

1. Automatic sprinklers--extra hazard pipe schedule or 25 gal/min per 5,000 sq. ft;
2. Curbing, ramps, or grating--covered trenches at floor opening in walls;
3. Low-level exhaust ventilation;
4. Explosion-proof electrics and adequate bonding; and liquids a
5. Adequate drainage leading to a safe disposal point.

Smoking and carrying matches, lighters, and other spark-producing devices should not be permitted in a building or area where flammable liquids are stored, handled, used, or where loading and unloading operations are performed. The extent of the restricted areas depends on the type of products handled, the design of the building, and, of course, State and local conditions.

Static Electricity

Static electricity is a motionless charge generated by the contact and separation of dissimilar material. For example, static electricity is created when a fluid flows through a pipe or from an orifice into a tank.

The principal hazards created by static are those of fire and explosion caused by spark discharges of accumulated electric charges in the presence of flammable or explosive vapors or gases. A spark between two bodies occurs when there is not a good electrically conductive path between them. Therefore, it is necessary to ground and bond flammable liquid containers in order to prevent static electricity from causing a spark. Points of great danger from a static spark are those places where flammable vapor may be present in the air, such as the outlet of a flammable liquid fill pipe, a delivery hose nozzle, near an open container of flammable liquid, and around a tank truck fill opening or barrel bunghole.

The terms bonding and grounding are often used interchangeably because of poor understanding of their functions. Bonding is done to eliminate a difference in potential between objects. The purpose of grounding is to eliminate a difference in potential between an object and ground.

To avoid a spark from discharge of static electricity during filling operations, a wire bond should be provided between the storage container and the container being filled. For additional safety, it is advisable to have the bonding wire on one of the containers grounded. When loading or unloading tank cars through open domes, it is best to use a downspout long enough to reach the tank bottom.

Friction sparks from metal tools are also possible. Spark-resistant tools should be used in the presence of flammable vapors.

Ventilation

Ventilation is an essential safeguard against flammable liquid fires and combustible explosions. With many flammable liquids, ventilation is also a vital health safety measure. Usually, the ventilation required for health safety is more than enough for fire and explosion safety.

Toxic Effects

Flammable liquids and their vapors may create health hazards from both surface contact and inhalation of toxic vapors. Inflammation results from the solvent action of many flammable liquids on the natural skin oils and tissue. A toxic hazard of varying degree exists in practically all cases, depending on the concentration of the vapor.

Many flammable vapors are heavier than air and will seek low points such as elevator pits, tank openings, and confined areas, which then contaminate the normal air and cause a toxic atmosphere. Oxygen deficiency occurs in containers that have been closed for a long time, e.g., tanks. All containers should be air- and gas-tested before entry.

Combustible Gas Indicators

Unless tests prove otherwise, flammable and toxic mixtures should be assumed to be present in all tanks that at any time have contained or have been exposed to flammable liquids. Tests for flammable vapor-air mixtures in tanks or other vessels may be made by chemical analysis of samples or with a combustible gas indicator, and usually may be read in terms of lower explosive limit (LEL).

A tank, tested before being cleaned, may be found vapor-free. However, if it contains scale or sludge, flammable liquids and vapor may be released as soon as the sludge or scale is disturbed. A safe rule to follow is that no tank should be considered free from the possibility of dangerous vapors as long as it contains scale or sludge.

Many companies use a written permit form when it is necessary for men to enter vessels that have contained flammable liquids or to do "hot work" repairs in them. We at Borden call our forms Hazardous Work Permits.

The criteria of safety relating to toxic hazards are not so strictly defineable as limits of flammability. Threshold Limit Values (TLV) based on past experience are published by many authorities. One of the best sources is Documentation of the Threshold Limit Value for Substances in Workroom.* Threshold limit values refer to airborne concentrations of substances to which nearly all workers may be repeatedly exposed day after day without adverse effect. Whereas the lower limits of flammability of most organic vapors are not less than 0.5 percent by volume, many substances are toxic in the parts per million range. Threshold limit values refer to time-weighted airborne concentrations of substances for an 8-hour workday and 40-hour work week. They should be used as guides in the control of health hazards.

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*Third edition, 1971, American Conference of Governmental Industrial Hygienists, P.O. Box 1937, Cincinnati, Ohio 45201.

One way to aid in this control is through the use of ventilation. To some, the placing of a fan to blow the vapors around and disperse it or to put a window fan near the location where the vapor is produced means ventilation. Generally, a ventilation system means exhaust fans with hoods and ductwork and makeup air to replace that being exhausted. It is wise to check when a ventilation system has been installed and to keep a running record of how it works. This can be done by periodically remeasuring air velocities at designated points and noting whether the system is functioning as well as it did when it was installed. Fans get dirty and lose blades; ductwork gets holes punched in it; fan belts loosen or break; all these lessen the efficiency of a ventilation system. Caution must be taken during cleaning, renovating, and reinstalling of fan motors as often miswiring occurs and fans push rather than pull. Watch for location of exhaust and intake for air conditioning or makeup air. Where ventilation cannot reduce air contaminates, it may be necessary to use respirators, self-contained breathing apparatus, or continuous-flow air supply.

Federal and State standards determine the levels of air concentrations an employee may be exposed to, at or above the action level, where action level is defined as one-half the permissible exposure level. If dealing with toxic materials like VCM and operating above the action level, recordkeeping and monitoring are required.

Recently, the Federal Government has issued proposed rules for toxic substances involving ketones. The proposed standards, if adopted, will establish requirements for measuring employee exposures, medical surveillance, methods of compliance, handling and use, employee training, recordkeeping, and so on.

Methyl ethyl ketone (MEK) is one solvent probably used in some quantity by each of you. If the proposed rules are approved, employer controls would be required for employees exposed to average airborne concentrations of MEK in excess of 200 ppm over an 8-hour work shift. These controls include exposure determination and measurement training and information, medical surveillance, personal protective equipment, improvements in the prevention and cleanup of spills and in monitoring disposals, and of course, recordkeeping. Approval of the proposed rules could also involve the use of engineering and work practice controls to reduce exposures to the permissible exposure levels or below. These are just a few of the proposed controls for toxic substances, and you can be sure there will be more.

Conclusion

I have tried to keep this simple and to the point. I hope you can benefit from what has been said on toxic and flammable chemicals used in the industry. There is a big job to be done, and it is time to get on with the job.

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DISCUSSION

DR. WILLIAM S. BEGGS (New Jersey Department of Environmental Protection, Trenton, New Jersey): I wonder if you could tell us what adverse effects the ketones have been found to provide. You mentioned methyl ethyl ketone.

MR. HELLER: Right.

MR. BEGGS: Can you tell us something about the effects of it?

MR. HELLER: The question is, what are the effects of methyl ethyl ketone?

To date, there has not been, to my knowledge, any substantial information to pinpoint the exact effects of ketones like those of the standards of VCM, vinylchloride monomer. There are hearings going on in Washington at the moment on the full ketone standards being proposed. Industry is really going back and forth with this as to what will be done. Who really knows? I think that there are going to be some limitations on the MEK, but what the standard outcome will be, I cannot say at this point. I expect that probably we will hear something around the first of the year or right after the first of the year.

MR. ALVIN SALTZMAN (New Jersey Bureau of Solid Waste Management, Trenton, New Jersey): With regard to methyl ethyl ketone, is the problem mainly with breathing or does it affect the contact with skin?

MR. HELLER: It is both. It is contact with the skin and also the breathing atmosphere that the proposed standard is referring to.

MR. SALTZMAN: Thank you very much.

MR. HELLER: Some people in industry are presently almost bathing in the MEK material. And what they are proposing there is a protective cream and gloves to use instead of--

MR. SALTZMAN: Yes, I am aware of that. That is why I posed the question. I know that everyone--a lot of people--are using it. They have their hands right in it. They are doing it every day.

MR. HELLER: You should have either a protective cream or probably both protective cream and gloves, but some gloves will break down with the solvent material.

MR. WILLIAM A. MAGIE (Magie Brothers Oil Company, Franklin Park, Illinois): I think that in the Federal Register they have changed the definition of flammable to 100°, and combustible under 200° instead of 140°.

MR. HELLER: You are right. I'm sorry. I was citing the definition by the NFPA. That was OSHA. Those who may be familiar with the Department of Transportation regulations, these are also a little bit different. They are trying to be all brought into one particular standard, which I foresee in the near future.

CHAIRMAN SCHAEFFER: Any other questions?

MR. JOHN H. SOMMER (General Formulations Co., Div. of General Research, Inc., Sparta, Michigan): I'd like to add a little something about static. We do a lot of dissolving and pre- and post-mixing from milling operations. We find that when we put a can under the dissolver, we develop a high rate of static electricity, probably on the order of 30,000 to 50,000 volts. So we ground the mixing tank.

MR. HELLER: Grounding the mixing tank will do it. If you are flowing anything from that tank to another container, you can break down the static charge by using some nonconductive material or hose to drop it through rather than a gravity flow; you can drop it through a closed system. There are flexible materials that will move from one area to another.

CHAIRMAN SCHAEFFER: Are there any other questions?

MR. A. MERLE SCHNITZER: (Phillips Petroleum Company, Bartlesville, Oklahoma): There are some additives that are available which can be added to some of the combustible material; I am not sure about the flammables, which tend to overcome the static electricity. There are agents that are used in jet fuels for fueling of aircraft. So this might be an angle you might want to look into if you have a problem in that respect.

The draft standards for ketones were mentioned, and although this is an EPA meeting, I think that everyone should be aware of the requirements that are being proposed in the OSHA area. They eventually will cover all of the materials that are listed in OSHA's table, in Section 1910. This is about 300 or 400 chemicals. It is going to be an enormous administrative task to keep up with. And everyone who handles these chemicals is going to be involved.

You have the opportunity of commenting upon these draft standards and it might be worth your while to look into them. The costs are going to be rather sizable, particularly if they apply to materials they really do not present that much of a problem. It is important that we concentrate on the real hazards and not spend a lot of time and effort and money where the problem really is not that great.

The vinylchloride thing is a real problem, and attention is being given to that but the costs in complying with these are going to be substantial. I don't think that industry or printing companies are going to be able to bear the entire burden. So the costs are going to have to be passed on to the consumer. That needs to be understood.

Another point is that in these draft standards you are required to set up certain surveillance at a level of half the TLV value. In other words, if you are at half, say, you are going to have to go into a surveillance program. And there are people who think this should not be required until you are at the TLV value, which is considered to be the safe value.

MR. HELLER: Half the TLV value or permissible exposure value is usually referred to as the action level.

HEAVY METAL CONTAMINATION IN PRINTING PAPERS

Robert W. Praskievicz*
and S. S. Y. Subt

Abstract

A method is described in which samples of printing papers are analyzed for trace contaminations of selected heavy metals. Three major categories of paper samples were tested, one of which was paper made entirely from or partially from recycled fibers. Recycled papers showed higher levels of chromium, copper, lead, and nickel contamination than did papers made from virgin pulp. Kraft wrapping papers made mainly from unbleached kraft pulp showed the highest levels of cadmium and manganese contamination. A "typical" printing paper is defined in terms of ranges of impurities. About 80 percent of the samples tested fall within these limits. Precision studies showed chromium, copper, manganese, and lead to be evenly distributed in the samples, while cadmium and nickel were not distributed uniformly.

INTRODUCTION

Work has been published treating separately the topics of determining the inorganic impurities in cellulose by atomic absorption spectroscopy (ref. 1) and of the use of the graphite furnace atomizer and atomic absorption spectroscopy to detect and measure metallic elements.

In this study, trace amounts of selected metallic impurities in printing paper are determined by the use of the graphite furnace. This investigation utilizes the general method of preparing the paper samples for analysis as described in a proposed revision of the Technical Association of Pulp and Paper Industry (TAPPI) Standard Method, T-436. This proposed revision expands the procedure to include other metals.

Use of the graphite furnace offers the ability to detect minute amounts of heavy metal contaminants by using samples only a few tenths of a gram in size. In this study an attempt is made not only to measure the amount of contamination but also to observe the distribution of the types of metals found in different kinds of paper.

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*Robert W. Praskievicz, Chemist, Quality Control and Technical Department, U. S. Government Printing Office, Washington, D.C.

Of particular interest are the heavy metal contaminants in the increasingly used recycled papers. The trend today is to define recycled papers as those which contain "post-consumer waste," i.e., paper that has been through its intended purpose, as distinguished from reclaimed fibers, which are obtained from waste collected as a result of an agricultural or manufacturing process and which include materials generated from and reused within a paper mill as part of its own papermaking process or as waste from a printing plant. Before most waste papers are suitable for recycling into printing papers, they must be treated to remove objectionable ink and other foreign materials.

In this project we investigated several recycled papers for foreign materials, specifically the heavy metals Cd, Cr, Cu, Mn, Ni, and Pb, and compared their concentrations to those found in other groups of printing papers.

EXPERIMENTAL

Sample treatment

All glassware used in this study was washed with concentrated or 1:1 nitric acid and then received successive rinsings with distilled and deionized water. A.C.S.-grade reagents were used throughout. The sample size used was 0.25 g. Pieces of each sample approximately 1 cm^2 in size were soaked in 5 ml of 30 percent hydrogen peroxide solution. They were then carefully added, using polyethylene tongs, to a heated mixture of 10 ml concentrated sulfuric acid and 5 ml 30 percent hydrogen peroxide. After the entire sample was dissolved, it was heated to dense fumes and allowed to cool. If the residual liquid was brown or cloudy, an extra 2 to 3 ml of 30 percent hydrogen peroxide solution was added, and the sample was reheated to dense fumes. This precedure was repeated until the residual liquid was clear or colorless. The sample was then cooled with ice and diluted with approximately 40 ml of deionized water. Then 20 ml of concentrated ammonium hydroxide were added dropwise to raise the pH to approximately 2. After filtering through #541 filter paper to remove any SiO_2 present, the sample was diluted to 100 ml with deionized water.

Ash determinations were made by heating 2-gram samples in porcelain crucibles to constant weight in a muffle furnace at 900° C.

Equipment

The instrument used was a Perkin-Elmer model 403 double-beam atomic absorption spectrophotometer equipped with a model HGA-2100 graphite furnace and a strip-chart recorder. Hollow cathode lamps were used for each element. Introduction of the sample and standards was by means of a 10-μl Eppendorf pipet.

Instrument parameters

Instrumental parameters used were essentially the same as those recommended by the manufacturer (ref. 2). Table 1 summarizes the conditions used.

Table 1. Instrument parameters

	Element					
	Cd	Cr	Cu	Mn	Ni	Pb
Hollow cathode current	8 ma	30 ma	30 ma	30 ma	30 ma	8 ma
Wavelength	2288 Å	3579 Å	3247 Å	2795 Å	2320 Å	2833 Å
Slit width	0.7 nm	0.2 nm	0.7 nm	0.2 nm	0.2 nm	0.7 nm
Drying temperature	100° C.	100° C.	100° C.	100° C.	100° C.	100° C.
Drying time	10 s	10 s	10 s	10 s	10 s	10 s
Charring temperature	500° C.	1100° C.	900° C.	1100° C.	1100° C.	500° C.
Charring time	30 s	20 s	20 s	20 s	20 s	30 s
Atomization temperature	2100° C.	2700° C.	2700° C.	2700° C.	2700° C.	2300° C.
Atomization time	10 s	10 s	10 s	10 s	10 s	10 s
Optimum working range observed	0.01 →0.10 ng	0.05 →1.0 ng	0.05 →0.50 ng	0.05 →1.0 ng	0.20 →1.0 ng	0.05 →3.0 ng

Standards and Calibration

Most standard solutions were prepared by diluting atomic absorption standards of 1,000-ppm concentration available from Fisher Scientific Company. The exceptions were lead, prepared from $Pb(NO_3)_2$, and chromium, prepared from $K_2Cr_2O_7$.

Ideally, the graphite furnace response is calibrated using known concentrations of metals in aqueous or in very dilute (< 1 percent) acid solution. The peak height or area of the recorder response is plotted versus the concentration of the element being analyzed. However, when a direct comparison is made between dilute aqueous standards and samples having a complex matrix, as in this investigation, chemical interferences may occur. Therefore, the calibration curve is run by adding known amounts of each element to the sample. This is called the standard additions method and is illustrated in figure 1 for chromium. If the slope for the

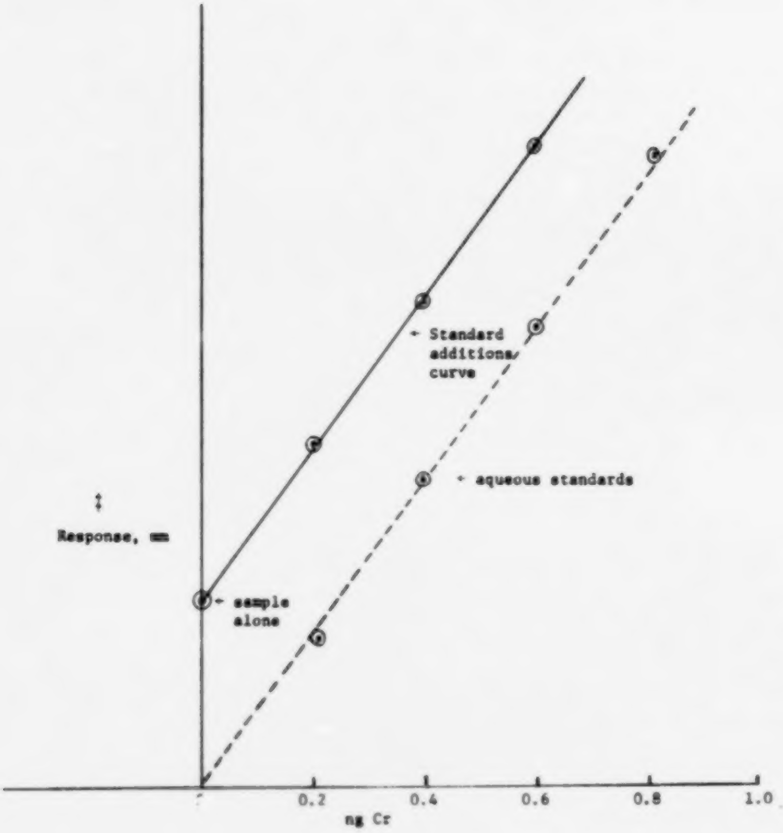

Figure 1. Method of standard additions.

standard additions curve is the same as the slope for the "standards only" curve, then the samples can be analyzed by direct comparison with aqueous standards. This relationship was studied for each of the six elements. All results reported were obtained by comparing the sample solutions directly with aqueous standards. In addition, the quantity of sample and standard solutions injected into the graphite furnace was always 10 μl to prevent any variations in signal due to volume effects.

RESULTS AND DISCUSSION

The results of analyzing 26 paper samples are grouped and shown in tables 2 through 5.

These (4) groups include:

Group I	One hundred percent bleached chemical wood paper. This group of printing papers includes offset book papers made from 100 percent virgin chemical wood pulp.
Group II	Recycled or partially recycled papers. This group includes paper made from 100 percent recycled fibers or some combination of recycled fibers with virgin chemical wood pulp or with cotton fibers.
Group III	Groundwood papers. In this category the papers are made from a mixture of groundwood pulp, which is a mechanically processed fiber, and chemically treated chemical woodpulp.
Group IV	Miscellaneous. This is the catch-all category containing kraft papers (similar to grocery bags), a hardened ashless #541 filter paper, and a 100 percent cotton fiber paper. The outstanding feature in kraft paper is that it contains some amount of unbleached chemical wood pulp treated by the kraft process, which gives this type of paper its strength characteristics.

Besides analyzing for the six heavy metals, the ash content was also determined for each of the samples. The ash is indicative of the noncellulosic material or inorganic fillers found in each paper.

On examining the results, note that these heavy metals occur in detectable quantities in every type of printing paper and that their concentrations vary over a large range. This is true even for the high-grade 100 percent rag content paper. Since a blank, ashless, acid-hardened

Table 2. Group I: 100 percent bleached chemical wood papers

Element (ppm or µg/g sample)	1	2	3	4	5	6	7	8
Cd	<0.2	<0.2	<0.2	0.2	<0.2	<0.2	<0.2	<0.2
Cr	5.9	6.9	13.5	8.9	1.0	13.2	14.5	10.8
Cu	5.1	6.4	3.7	2.4	7.3	3.0	2.6	1.8
Mn	2.1	1.0	3.6	11.9	1.1	<1.0	2.8	10.6
Ni	8.8	11.0	6.7	5.4	5.3	15.5	14.9	16.2
Pb	2.3	1.0	7.2	7.7	11.5	2.9	5.5	5.8
Ash	10.0%	9.5%	12.0%	7.0%	9.5%	12.0%	16.5%	14.5%

Table 3. Group II: Recycled or partially recycled papers

Element (ppm or µg/g sample)	9	10	11	12	13	14	15	16
Cd	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Cr	35.1	13.3	19.7	2.1	7.9	20.0	10.8	3.1
Cu	76.6	1.4	11.0	<1.0	3.4	<1.0	4.0	2.5
Mn	4.3	4.2	3.5	21.8	2.2	2.1	7.6	<1.0
Ni	37.6	7.2	7.2	<1.0	4.4	17.4	5.4	5.9
Pb	76.9	8.4	58.5	<1.0	3.9	2.0	6.4	3.1
Ash	7.5%	9.5%	9.5%	9.0%	6.5%	21.5%	2.0%	3.0%

Table 4. Group III: Groundwood papers

Element (ppm or µg/g sample)	22	23	24	25	26*
Cd	<0.2	<0.2	<0.2	<0.2	<0.2
Cr	16.6	19.4	14.3	<1.0	22.1
Cu	<1.0	<1.0	2.2	3.2	2.9
Mn	13.0	12.1	8.6	19.1	6.7
Ni	14.7	10.5	8.2	<1.0	6.2
Pb	<1.0	<1.0	<1.0	<1.0	96.5
Ash	18.0%	13.5%	8.5%	0.5%	5.5%

*26 can also be classified with the recycled papers.

Table 5. Group IV: Miscellaneous papers

Element (ppm or µg/g sample)	17 Kraft	18 Kraft	19 Kraft	20 Filter paper	21 100% rag
Cd	3.5	0.9	0.2	<0.2	<0.2
Cr	10.7	3.7	1.8	<1.0	4.3
Cu	2.2	20.0	8.4	<1.0	5.2
Mn	51.5	36.4	37.4	<1.0	<1.0
Ni	1.3	4.5	4.1	1.7	<1.0
Pb	35.9	14.2	3.0	2.6	2.4
Ash	2.0%	1.0%	0.5%	<0.02%	<0.5%

filter paper was analyzed and found to contain some of the same heavy metals, we suspect the impurities found in this paper may be from the acid-hardening process (table 5, sample #20).

In table 6, the low, high, mean, and standard deviation are shown for the contaminants of Groups I, II, and III, and an "overall" result is given for the 26 samples analyzed. The results may not show any definite or obvious conclusions, but with a closer examination there are some interesting trends to be obtained from this study.

In general, for any group of paper samples containing inorganic fillers, the nickel and chromium content is proportional to the filler content. These fillers are added to improve the brightness and opacity. Except for a few instances, these results are summarized in table 7.

Table 6. Summary of contaminants

	Overall				Group I: 100% bleached chemical wood				Group II: Recycled				Group III: Groundwood*			
	Low	High (ppm)	Mean	Std. dev.	Low	High (ppm)	Mean	Std. dev.	Low	High (ppm)	Mean	Std. dev.	Low	High (ppm)	Mean	Std. dev.
Ash	<0.02	21.5	8.0	5.9	7.0	16.5	11.4	3.0	2.0	21.5	8.6	6.0	0.5	18.0	9.2	6.8
Cd	<0.2	3.5			<0.2	0.2			<0.2				<0.2			
Cr	<1.0	35.1	10.8	8.2	1.0	14.5	9.3	4.6	2.1	35.1	14.0	10.8	<1.0	22.1	14.6	8.2
Cu	<1.0	76.6	6.9	14.8	1.8	7.3	4.0	2.0	<1.0	76.6	12.6	26.1	<1.0	2.9	2.1	1.0
Mn	<1.0	51.5	10.3	13.1	<1.0	10.6	4.3	4.4	<1.0	21.8	5.8	6.8	6.7	19.1	11.9	4.8
Ni	<1.0	37.6	8.6	7.7	5.3	16.2	10.5	4.6	<1.0	37.6	10.8	11.3	<1.0	14.7	8.1	5.1
Pb	<1.0	96.5	14.0	25.0	1.0	11.5	5.5	3.4	<1.0	76.9	20.0	29.9	<1.0	96.5	20.1	42.7

*Includes sample #26, which may also be classified as a recycled paper.

Table 7. Offset book papers

	Contaminants, average concentration, ppm				
Ash content	Cu	Mn	Pb	Cr	Ni
0-10%	5.3	4.0	5.6	5.7	7.6
> 10%	2.8	4.5	5.4	13.0	13.3

Also, on the average, the higher quality printing papers (100 percent bleached chemical wood fibers) contain the least amount of the sought-for heavy metals except nickel (see table 6).

The cadmium levels were numerically low, only 4 out of 26 samples showing a concentration of 0.2 ppm or better. Of particular interest is that three of these four samples are kraft paper samples. These same samples are also consistently high in manganese. Each was higher than the maximum manganese concentration of 21.8 ppm observed in the other 22 samples.

Besides kraft papers, two other samples having a high manganese content are duplicator papers. One is composed of groundwood fibers and the other of recycled fibers. Excluding the kraft and duplicator-type paper samples, the remaining 21 samples show a maximum manganese contamination of 13.0 ppm.

Based on our results, a "typical printing paper" has heavy metal contaminants in the following concentrations: Cd, <0.2 ppm, Cr, <15 ppm, Cu, <10 ppm, Mn, <15 ppm, Ni, <15 ppm, and Pb, <15 ppm. Approximately 80 percent of the paper samples analyzed fall within these limits.

But what about the remaining 20 percent of the papers? The high concentrations of manganese and cadmium in kraft paper were noted earlier. High concentrations of the remaining impurities--chromium, copper, nickel, and lead--seem to be distributed among the papers with recycled fibers.

The heavy metal contamination among the recycled papers appears to decrease as these papers are subjected to bleaching or other refining processes that make the paper visually appealing. Samples #9 and #26 have low brightness and specks of foreign material giving a spotty "recycled" appearance. These samples show some of the highest levels of Cr, Cu, and Pb of all the samples tested. Conversely, samples #13, #14, #15, and #16 had high brightness, a clean appearance, and low amounts of the above impurities.

Studying the results for the nine recycled papers,* an interesting observation is that none of these samples shows both a high manganese and a high lead contamination. These elements were once commonly used in combination in ink formulas as driers and one might suspect high concentrations of these two elements in recycled paper. Sample #10 is known to be composed of de inked stock and had neither high Mn nor high Pb concentrations. Returning to samples #9 and #26, these two recycled papers were detected to have the highest Pb contamination but to have a low concentration of Mn. Strangely enough, the combination of high Mn and high Pb only occurs in the kraft paper samples.

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*Including sample #26, which is composed of recycled and groundwood fibers.

Precision

Five replicate samples were wet-ashed and analyzed for each of the six elements. A 100 percent recycled paper was selected for Cu, Cr, and Ni precision studies. For Mn and Cd, a kraft wrapping paper was used. The results obtained are shown in table 8. The precision for Cr, Cu, and Mn

Table 8. Results of five replicates of the same paper sample (ppm)

Replicate sample	Cd	Cr	Cu	Mn	Ni	Pb
1	4.04	35.1	74.8	49.8	8.03	78.0
2	7.39	34.6	78.5	47.2	7.02	66.0
3	4.42	37.1	76.6	51.9	7.69	80.5
4	4.04	34.2	72.9	53.4	6.35	86.9
5	3.52	34.6	80.4	55.0	13.6	73.1
mean = $\overline{x}$	4.682	35.12	76.64	51.46	8.538	76.90
variance = s^2	2.394	1.327	8.743	9.348	8.423	61.86
standard deviation = s	1.547	1.152	2.957	3.057	2.902	7.865
coefficient of variation = $\frac{100s}{\overline{x}}$ (parts per hundred)	33.1	3.28	3.86	5.94	34.0	10.2

was relatively good, indicating that these elements are evenly distributed throughout the samples. The relatively high variance for Cd, Pb, or Ni indicates that these are not as uniformly distributed. To further impede precise Ni determinations, the observed Ni content approaches the detection limit of the instrument, where the signal to noise ratio is high. Under the experimental conditions, the observed detection limit for a 0.25-g sample is approximately 4 ppm, as compared to less than 0.5 ppm for copper.

CONCLUSION

This investigation was undertaken at the U. S. Government Printing Office for several reasons, not the least of which was to develop data on possible toxic materials in our products in order to provide answers to increasingly numerous questions from Congress and Governmental agencies. While some results may be surprising, they must be viewed in perspective. The results of some of the heavy metal contaminants are numerically high but the units are small. In the extreme case, it would require more than 10 kg (over 22 lb) of paper to provide 1 g (1/28 ounce) of lead. For comparison, the amount of lead permitted in coatings for children's toys and furniture is 0.06 percent or 600 ppm (ref. 3). There is no question that sources of toxic materials should be investigated, but all that one can conclude from this study is that it would be prudent to investigate how lead and other heavy metals get into consumer papers.

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2. Analytical Methods for Atomic Absorption Spectrophotometry, Perkin-Elmer Corporation, Norwalk, Connecticut, 1968.

3. "Rules and Regulations," title 16, chapter II, Consumer Product Safety Commission, Part 1500 - Hazardous Substances and Articles; Administration and Enforcement Regulations, Federal Register, Vol. 39, No. 237 (December 9, 1974), p. 42902.

DISCUSSION

MR. THEOPHILUS R. CARSON (Food and Drug Administration, Washington, D.C.): What was the sensitivity, if you can remember, for cadmium and lead?

MR. PRASKIEVICZ: In the case of cadmium, for a .25-g sample, we could detect with pretty good precision down to about .2 ppm. We diluted our samples to 100 ml. You could dilute some to a smaller volume and increase your sensitivity. Or you could easily go to a larger size sample. In fact, when we started the study, we were using 1-g samples or higher, but we found that we had to dilute the samples for most of these elements, to get them into the proper working range. So, you could easily get down. I would not want to venture a guess, but I would say maybe .02 ppm. I would say you could easily go 10 times below that with a scale expansion factor of 10.

MR. CARSON: I asked you that because we have seen much lower values from a food additives standpoint than what you have given here.

MR. PRASKIEVICZ: Well--

MR. CARSON: Certainly for the safety of food additives we could not tolerate that kind of a lead content.

MR. PRASKIEVICZ: As I say, this type of paper is not used for wrapping food. These are strictly printing papers. This technique would definitely be applicable to papers that do come in contact with food.

MR. JOHN SANDEFUR (Hallmark Cards, Kansas City, Missouri): The first point was simply that the Consumer Products Safety Commission on lead in coatings is a half-percent at this time, I believe.

MR. PRASKIEVICZ: Okay. Well, the figure that we used was out of the *Federal Register* that appeared February 9, 1974. It did list .06 percent.

MR. SANDEFUR: That was dropped. I wanted to ask if on your initial paper sample the weight was recorded on a dry basis?

MR. PRASKIEVICZ: The samples were equilibrated at a 50 percent relative humidity. So they were not on a dry basis. They were at equilibrium moisture.

MR. SANDEFUR: So you may be carrying several percent moisture?

MR. PRASKIEVICZ: Probably. Another thing that could have affected some of the precision results that we did have...

MR. SANDEFUR: Was background friction required?

MR. PRASKIEVICZ: No. We started out running with background correction, but we found that most of these elements ran pretty well without it. With this sample matrix there does not seem to be any problem with background. At least we did not run into it.

MR. RONALD G. RAYNER (Department of Environmental Protection, Coventry, Connecticut): In the industries that employ the inking process, did you happen to notice the tendency toward fewer metals in those that had the inking?

MR. PRASKIEVICZ: Well as I say, the only sample that we knew was actually made from Dean stock, was that one sample that I pointed out to you. The levels were fairly low. We are assuming that most of these other recycled papers did use a certain amount of deinked stock. But of course, this kind of information is not that easy to come by. For the purpose of this study, we did not really go into any great details.

MR. RAYNER: You say for recycled paper. We have several industries that employ recycling of papers, and one of them makes a filler for corrugated medium, for cardboard boxes--a very cheap grade of paper, not employing the kraft process. Did you also happen to notice a tendency there for your TDS increase in being recirculated throughout the system to develop into a higher metal concentration?

MR. PRASKIEVICZ: No, we did not investigate that.

MR. FRANCIS M. ALPISER (Environmental Protection Agency, Philadelphia, Pennsylvania): I wonder if you analyzed any money? We have had requests from the Treasury Department about burning money. That is a fact in Washington, D.C. They want to burn it in an incinerator with no kind of control. And I wonder what the metal content of money is.

MR. PRASKIEVICZ: We do not print the money. That is the Bureau of Engraving and Printing, but it would make an interesting study.

THE FLOOR: What category would you expect to find it in?

MR. PRASKIEVICZ: As I understand it, it is a ragtype of paper.

MS. JACQUELINE M. FETSKO (Lehigh University, Bethlehem, Pennsylvania): I gather that your measurements are on total lead. Are you planning any studies of soluble lead? Leads must be acid-soluble to be absorbed into the digestive tract of the body.

MR. PRASKIEVICZ: Right. That is definitely something to consider.

THE FLOOR: What was the question?

CHAIRMAN SCHAEFFER: Will you paraphrase, Bob?

MR. PRASKIEVICZ: I think the point she was trying to make was that some forms of lead may not be soluble in the particular acid mixture that we use here. So, that in--

CHAIRMAN SCHAEFFER: This was really an analysis of total lead. Have you attempted to differentiate between soluble lead as opposed to total lead, because of the acid involvement in the extractability for lead ingestion and that potential danger?

MR. PRASKIEVICZ: No, we have not investigated that as yet.

PROCESSING EFFLUENT CHARACTERISTICS OF DYCRIL* PHOTOPOLYMER PRINTING PLATES

Ellen G. Mellinger†

Abstract

The Du Pont Photo Products Department markets a whole family of letterpress printing plates based on photopolymer technology. A photopolymer is an organic plastic material that hardens and becomes insoluble when exposed to UV radiation and which, in the case of Dycril plates, has been bonded to a rigid or flexible support, depending on the application. After exposure Dycril plates are washed in dilute aqueous alkali. Several years ago a program was undertaken to characterize the water pollution potential of the Dycril washout effluent. The paper describes photopolymerization in general terms and the Dycril printing plate exposure and washout process. The results of the Dycril effluent analysis are given and reviewed in light of Federal regulations and municipal sewer system codes. It is concluded that Dycril does not present a pollution problem when discharged to a municipal sewer system.

INTRODUCTION

The Du Pont Company Photo Products Department sells Dycril platemaking processes to various customers throughout the world. The processes are based on photopolymer technology, representing a distinct environmental advantage over the metal-etching process and its attendant problems with zinc, copper, and their salts. With increasing and continuing concern for the environment, the Photo Products Department several years ago undertook a program to characterize the water pollution potential of its Dycril photopolymer effluent.

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*Dycril is a registered trademark of E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware.

†Technologist, Photo Products Department, E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware.

POLYMERIZATION/EXPOSURE STEP

In order to more fully understand photopolymer effluent, let us discuss in general terms what a photopolymer is, how it reacts, and what the processing conditions are. A photopolymer is an organic plastic material that is sensitive to UV radiation. In the cross section of a Dycril photopolymer plate (illustrated in figure 1), the photopolymer is the solid layer, which has been bonded to a suitable support. The choice of support is determined by the end use: rigid for flat bed or rotary letterpress and flexible for wraparound letterpress and letterset printing. Thickness of the photopolymer is also a function of the end use and varies from .010 in. to .150 in.

The polymer layer in a typical plate contains an inert organic material to give film-forming properties (this is the solid binder), a plasticizer monomer (capable of forming a polymer), and a photoinitiator or catalyst to give the required photo speed, plus other organic compounds in lesser amounts, such as polymerization inhibitors for storage stability.

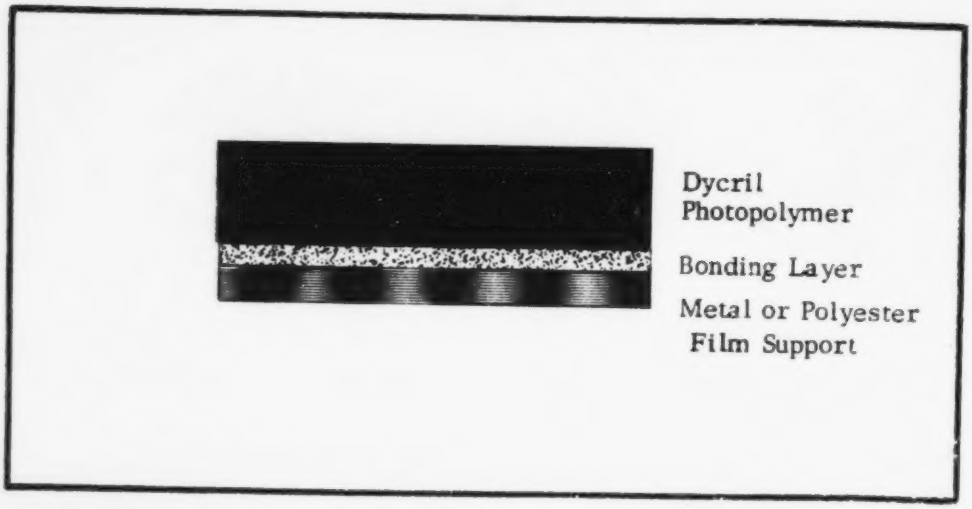

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Figure 1. Dycril plate cross section.

Synthetic polymers are formed by chemical reactions in which a large number of small units (monomers) combine to form one large unit (the polymer) as shown in figure 2. The source of energy for this reaction in Dycril is ultraviolet radiation. When the plate is exposed the photoinitiator triggers the linking and crosslinking of monomers to form a crosslinked polymer with different physical properties, such as hardness and durability. These modifications allow the polymer to withstand high pressure during matting in the newspaper process. In other applications it provides the plate with the necessary wear characteristics for long press runs. The hardened area is also inert to most inks and solvents used in the press room. The exposure step requires a high contrast film negative with high density (D-max of 3.7-4.0) in the black nonimage areas and with low density or D-min in the clear image area. A matte surface is also necessary to allow proper draw-down in the exposure unit, thereby eliminating trapped air pockets and obtaining good contact between plate and film. Without matte, the relief image will be distorted. This high-contrast negative is placed on top of the plate, which is then exposed to a UV source. The radiant energy is transmitted through the clear area and triggers the polymerization and hardening, while the monomer in the unexposed areas remains unchanged.

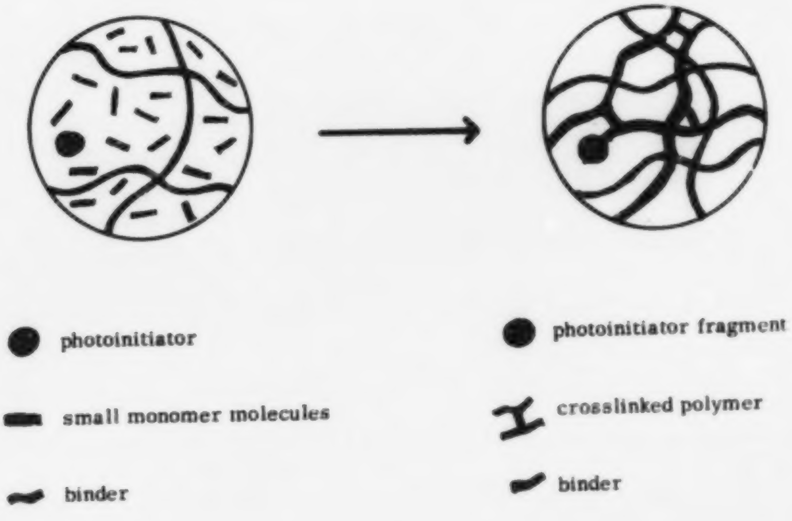

Figure 2. Photopolymer composition.

WASHOUT

The nonexposed areas are then washed away while the exposed areas remain in relief. The preexposed Dycril plate is sprayed with a dilute solution of sodium hydroxide at a temperature of about 85° F within a closed washout unit. Concentration of the solution is approximately 0.2 percent NaOH (about 0.036N), which is equivalent to about 6 fluid ounces of 50 percent caustic in 25 gallons of water and illustrates the dilute nature of this washout mixture. The concentrated caustic solution is typically stored in a 55-gallon drum and is pumped into the washout unit where it mixes with the proper amount of water. An automatic control minimizes operator exposure to the washout solution.

Each washout unit can handle two plates per washout cycle, resulting in an effluent of 3 to 4 gallons/minute or about 15 gallons/washout. Depending on plate production (see table 1) the flow from a Dycril installation can be as low as 100 gallons/day to as high as 2,000 gallons/day.

Total flow/day, then, is dependent on whether use is continuous or intermittent, as well as on the number and size of plates processed. To gain perspective let us relate gallons/day to number of washouts and number of plates. Most Dycril installations fall in the lower volume category of 100 gallons/day, which corresponds to about seven washout cycles and to the

Table 1. Dycril* installation
(flow 100 - 2,000 gal/day)

Gallons	Washouts	Plates
100	7	14
750	47	94
2,000	125	250

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processing of 7 to 14 plates. Probably a more realistic situation with most Dycril newspaper operations would be 750 gallons/day washout effluent corresponding to approximately 47 washouts or 94 plates. In the case of a large 24-hours-a-day, 7-days-a-week newspaper operation, maximum figures would be 2,000 gallons/day--equal to 125 washouts and 125 to 250 plates.

DYCRIL EFFLUENT

Visually, the Dycril washout effluent is an aqueous, colorless suspension of settleable solids that are very light and fluffy, much like a bulky activated sludge. Slight turbulence keeps the solids in suspension.

Samples taken directly from the washout unit after processing different plate types were sent to outside laboratories for analysis. In reviewing the results it was apparent tha the effluents were very similar regardless of the plate type, as would be expected since all plates are of approximately the same composition.

Table 2 presents the results from analyses of several washout solutions. The data in the table show that the washout solution has relatively high pH (11.0-11.5) as well as high BOD, COD, and suspended solids concentrations.

Table 2. Results from analyses of several Dycril* washout solutions (pH 11.0 - 11.5)

	mg/l	lb/day
BOD_5	1,700-2,600	11-43
COD	7,000-11,000	44-183
SS	2,500-3,000	16-50
Total solids	7,500-8,500	47-142
Heavy metals	None	
Flow	750-2,000 gal/day	

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However, it should be pointed out that these relatively high concentrations yield low quantities (lbs/day) of the pollutants being discharged.

Routine operation of the washout unit yields an effluent with no residual heavy metals. However, it should be noted that periodic acidic cleanups of the unit have resulted in residual copper and zinc levels during the cleanup period (about 20 minutes/month). The source of copper and zinc is believed to stem from acidic corrosion of brass fittings in the washout unit. These intermittent discharges of copper and zinc are considered to be negligible and result in a total of only 0.0003 lbs of copper or zinc being discharged during the acidic cleanup of a 35-gallon washout unit. Table 3 presents some other parameters that might be of interest and that were analyzed in the washout solution. The parameters are alkalinity, TOC, percent solids in suspension,* and settleable solids.

Table 3. Additional parameters analyzed in the Dycril* washout solution

	mg/l	lb/day
Alkalinity		
Phenolphthalein	215	1.3-3.6
Methyl orange	275	1.7-4.6
Total organic carbon (TOC)	3,200-3,500	20-58
% Solids in suspension - 30-40%		
Settleable solids - 600-700 ml/l		
Flow - 750-2,000 gallons/day		

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*The ratio of suspended solids to total solids.

REGULATIONS--FEDERAL

What do these numbers mean with respect to water pollution regulations?

Most Dycril users discharge to municipal sewer systems, and to gain perspective let us suppose that a relatively large-volume Dycril newspaper operation--1,000 gallons/day--discharges into a small municipal treatment system handling 1 M (Million) gallons/day. The flow, COD, BOD, and SS loading of the Dycril operation represents 0.1 percent, 5 percent, 2.0 percent, and 2.7 percent of the municipality's flow, COD, BOD and SS loadings, respectively. It should be noted that these calculations represent an extreme case of a large newspaper in a small town. A more typical situation would be the discharge of 1,000 gallons/day into a 10 M gallons/day municipal treatment operation. This case would reduce the Dycril effluent contribution by an order of magnitude, yielding 0.01 percent, 0.5 percent, 0.2 percent, and 0.3 percent for flow, COD, BOD, and SS loadings, respectively.

Even in the worst case of the operation contributing 2,000 gallons/day, it is not a major contributing industry as defined in EPA's Pretreatment Standards (40 CFR Part 128.124). However, it is important to remember that each situation must be analyzed separately and that these calculations should be done for each customer, based upon the figures specific to his case, in order to determine the magnitude of his contribution relative to the total municipal load. Dycril effluent also does not fall into any of the prohibited-wastes categories, as defined in the Pretreatment Standards. It is not a fire or explosion hazard, is not corrosive, is not solid or viscous, and is not discharged at a flowrate that is so excessive as to cause treatment process upset or loss of treatment efficiency.

REGULATIONS--STATE AND LOCAL

Municipal treatment plant discharges are subject both to Federal regulations and possibly to water quality standards. Thus, in addition to Federal pretreatment standards, most municipalities establish their own pretreatment limitations to protect their treatment system performance levels.

The analysis of Dycril effluent, when compared to allowable limits established in the past by some municipalities, suggests a violation of maximum limitations for some parameters, such as pH, BOD, and SS. However, most municipalities are modifying their sewer codes to accept compatible effluents. Compatible pollutants, as defined by EPA (Pretreatment Standards-40 CFR, Part 128.121) include BOD, suspended solids, and pH, plus other pollutants such as COD and TOC in appropriate situations. Pretreatment for removal of compatible pollutants is not required by current EPA regulations. Laboratory tests clearly show that the Dycril effluent contains biodegradable, compatible pollutants that can be treated and, therefore, accepted by a secondary municipal sewer system and which do not contain prohibited waste categories of materials.

Thus industrial compatible pollutants can be treated by a municipal treatment plant, but the discharger must pay his fair share of the treatment cost in the form of a surcharge. Surcharge schedules can be obtained upon request and are usually based on formulations, which take into consideration flow, suspended solids, and BOD above certain levels.

Typical surcharges might be \$0.03-0.05/lb of BOD and suspended solids and \$0.04/1,000 gallons of hydraulic flow. Thus, in the case of a 1,000 gallon/day Dycril operation, total daily surcharge cost would be on the order of \$2.20. This calculation again points out the small contribution that a typical Dycril operation would have on a municipal sewer system.

Should a customer require more specific data on Dycril effluent, table 4 presents an appropriate formula and factors that can be used to compute the parameters for total solids (TS), suspended solids (SS), COD, and BOD_5 from both 25- and 35-gallon washout units. The pollutant parameter expressed in mg/l, is equal to (the factor for that pollutant) X (percent washout) X (plate area) X (plate thickness). The effluent characteristics, then, of the washout of any Dycril plate can be easily calculated and are readily available to anyone.

CONCLUSIONS

In conclusion, we think it is reasonable to say that the Dycril system does not present a pollution problem when discharged to a municipal sewer system. Dycril operations yield low-volume, intermittent discharges that

Table 4. Specific data on Dycril* washout effluent

Pollutant Parameter [a]	Factor	
	25-gal tank	35-gal tank
Total solids (TS)	220	157
Suspended solids (SS)	130	102
Chemical oxygen demand (COD)	280	200
Biochemical oxygen demand (BOD_5)	130	102

*Dycril is a registered trademark of E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware.

[a] Pollutant parameter (mg/l) = factor × (% washout) × (plate area) × (plate thickness).

are biologically degradable, contain no heavy metals, and are therefore compatible with secondary municipal water treatment systems.

DISCUSSION

MR. ROBERT MASIULIS (Case-Hoyt Corporation, Rochester, New York): On these compatible pollutants, can you tell me what figures you are basing the allowable concentrations on? Because in my area, you would be over. They have a maximum five times, let's say, allowable BOD and COD for surcharge. And looking at the figures you had, you would be well beyond that, and that would require pretreatment.

MS. MELLINGER: I believe current EPA regulations do not require pretreatment. And secondary municipal sewer systems will charge for BOD and COD above a certain level. Is that your question?

MR. MASIULIS: I guess I am really referring to local regulations, because especially in our area, they have a limit of five times. BOD is 300 mg/l and COD is 600 mg/l. And five times would bring it above that. So I was curious as to what figures you were using--standard Federal regulations or any specific local regulations?

MS. MELLINGER: The figures presented were based on 100 percent washout of the plates and on the effluent as it comes out of the washout processor. The figures do not take into account that the amount of photopolymer washed out can vary with each plate and would never be 100 percent but rather would average about 50 percent. Therefore, the figures presented would be 50 percent less. Also, the figures do not take into account other wastewater sources in a building and possible dilution from them.

The surcharge figures as well as percent contribution figures were based on conservative (low) concentrations of BOD, COD, and SS considered to be acceptable to an average municipal treatment plant.

CHAIRMAN SCHAEFFER: I think we have the authority in the audience to answer the question as to EPA versus local agency requirements. Mr. King.

MR. ROBERT L. KING (Environmental Protection Agency, Denver, Colorado): I think the difference between what this gentleman suggested and what you are referring to is that the Federal regulations are as you stated it. The local regulations can be more stringent, but not less stringent then the proposed rules and regulations.

One caveat, I think, on your data is that 50,000-gallon limit is total flow. So, you may not be exact just because you use a Dycril plate. If you happen to be discharging any combinations greater than 50,000 gal/day in the municipal sewer, including noncontact cooling water, you can still be considered a major discharger. So, the Dycril plate is not going to save you from that possible problem. It is a very minor detail.

I am not trying to detract from the data, except that the fact that you have a Dycril plate does not make you a nonmajor discharger. It is total flow, regardless of the contaminant level.

MS. MELLINGER: Total building flow?

MR. KING: Right.

GENERAL CHAIRMAN FISHER: I just cannot resist making a comment here because it seems to me that this industry or any other is going to get in trouble if the game it is going to play is going to be to try and sneak under the regulations by a hair. The regulations will change with time. The Government may not be as bright as you are, but it eventually catches up.

I think what you really have to ask is whether this material environmentally is safe and whether our wastewater system is going to be able to handle it in the long run, rather than whether we can get around the regulation that happens to be in force today and go ahead and use it.

MS. MELLINGER: The intent is presenting this paper was not to "get around the regulation. . .in force today" but to share with you the characteristics of the Dycril effluent and to examine them in light of the regulations. Pretreatment studies of the Dycril effluent have been extensive but the expenses involved in setting up pretreatment facilities have not been justified at the present time due to the biodegradability and relatively small impact of Dycril effluent.

MR. K. C. GOEL (Richardson Associates, Dover, Delaware): I notice that pH on our effluent was 11.0 to 11.5. That seems pretty high. Can you comment on that?

MS. MELLINGER: Well, I did say in my paper that it had high pH. So we recognize that.

PLATEMAKING AND ITS EFFECT ON THE ENVIRONMENT

Steven Latus*

Abstract

Processing offset printing plates involves the use of various chemicals that can be detrimental to the environment. This paper will discuss the steps involved in making surface, deep-etch, hard metal, and wipe-on plates and those chemicals that are commonly used. It will also cover methods by which printing shops can pretreat their wastes before the wastes are discharged into sewer lines or otherwise disposed of.

Although there are many presensitized plates on the market today, this paper will concern itself mainly with surface, deep-etch, hard metal, and wipe-on plates. A step-by-step description of how each type of plate is processed will show us which chemicals are involved.

Surface plates, like deep-etch plates, are made of either zinc or aluminum. In the making of a surface plate, the plate is coated with a light-sensitive coating. When exposed through a negative, the image areas are hardened so that they will accept ink. The coating is then washed off of the nonimage areas, and these areas are made water-receptive by treatment with a desensitizing etch.

The first step in the making of a surface plate (and a deep-etch plate as well) is to counteretch it. This is essentially a cleaning process and usually involves the use of a dilute acid solution, although alkaline counteretches are occasionally employed. Phosphoric, acetic, hydrocholoric, and sulfuric acids are commonly used in dilutions of 1 to 4 oz/gal water. In the whirler or sink, the counteretch is poured onto the plate surface and is kept agitated by a bristle brush. After about a minute, the plate is rinsed liberally with water.

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*Project Leader, Lith-Kem Corporation, Lynbrook, New York.

The next step, preetching, is used primarily on zinc plates. The preetch solution is brushed over the plate surface, left on for about a minute, and then rinsed off with water. This solution usually is an acidified solution of gum arabic to which ammonium bichromate has been added. Preetching facilitates even spreading of the light-sensitive coating and also makes the plate develop out easier later on in the process.

After preetching, the plate is coated in the whirler with the surface-coating solution. This coating consists of a water solution of ammonium bichromate, a small amount of ammonia water, and a protein type of colloid such as egg albumin, casein, a modified casein, or soybean protein. The combination of ammonium bichromate and protein colloid makes the coating light-sensitive, while the ammonia water raises the pH of the solution to about 9. This high pH considerably slows down the natural reaction between the colloid and the ammonium bichromate and acts to preserve the useful properties of the coating while it is in the bottle.

After exposure in the frame, the coating is often covered first with a surface lacquer in order to give a longer run on press. This lacquer is a solution of resins in an organic solvent. Then the plate is covered with a developing ink, which increases the ink receptivity of the image areas of the plate.

To develop the plate, a dilute ammonia solution is used (about 1 oz ammonia water/gal water). This removes the unhardened nonimage areas. The plate is then washed off with water and squeegeed dry.

After development, a desensitizing etch is applied and allowed to dry. This desensitizing etch is an acidified solution of gum arabic, which may also contain dissolved salts such as ammonium bichromate or a nitrate. After the desensitizing etch is dry, a plain solution of gum arabic in water is applied and allowed to dry. The plate is now ready for the press.

It is plain to see that there are quite a few chemicals used in this process, which are undesirable from an ecological standpoint. The bichromate solutions contribute hexavalent chromium, a suspected carcinogen.

Many of the solutions contain acids or ammonia. During development, coating plus surface lacquer and developing ink are washed down the drain.

One obvious solution to prevent these various pollutants from reaching the municipal water supply is to hook up holding tanks to the sink and whirler drains. The hexavalent chromium can be reduced by lowering the pH of the tank to about 2 with a strong mineral acid (sulfuric or hydrochloric) and then adding a strong solution of reducing agent, usually ferrous sulfate or sodium bisulfite. This transforms the hexavalent chromium to the trivalent form. Mixing should be constant during the entire process in order to make the reactions take place as fast and as thoroughly as possible. Some companies use motors and some use compressed air to keep the solution in the tank thoroughly agitated. Before proceeding with the next step, you must determine that the hexavalent chromium level is below allowable limits for your area.

The Hach Chemical Company, Ames, Iowa, sells many different types of water analysis kits, which are moderately priced and easy to operate. After you have reduced your hexavalent chromium sufficiently, you can then proceed with neutralization of the tank waste. This involves adding a base such as caustic soda solution. You can raise the pH to a 6 or so and then contact a special scavenger service to properly dispose of the waste. The pH could also be raised to between 8 and 9, which will cause all of the metals in solution to precipitate out as hydroxide. Let the waste settle for a minimum of 8 hours, and filter it if necessary. The resulting liquid can be discharged into the community sewer system and settlings can be removed by special scavenger services.

The deep-etch process uses even more chemicals than does the surface-plate process. Deep-etch plates are exposed through a positive and are used when a long-running plate is desirable.

Like a surface plate, deep-etch plates are first counteretched with a dilute acid solution and rinsed with water. The plate is then coated in the whirler with deep-etch coating, which usually consists of a water solution of gum arabic, ammonium bichromate, and ammonium hydroxide.

After the coating is dried and the plate is removed from the whirler, it is exposed in the frame. After exposure, the plate is checked for blemishes or unwanted marks where light has been held back by dust, lint, etc. These areas will develop under the deep-etch developer unless they are covered with a stop-out solution. The stop-out solution consists of a shellac, varnish, or similar material dissolved in an organic solvent along with a dye or pigment. This solution must be able to withstand the developing and etching steps but dissolve readily in the alcohol wash, which is applied after etching.

After the stop-out has dried, the plate is developed. Deep-etch developer consists of a concentrated aqueous solution of metallic salts plus organic acids. This solution will remove the unhardened coating without attacking the exposed or hardened areas.

When development is complete, the next step is to deep-etch the plate. Usually this deep-etch solution contains ferric chloride along with other chlorides and a small amount of acid. This solution dissolves some of the metal in the image areas and thus makes these areas slightly depressed.

After etching for about a minute, the deep-etch solution must be removed completely from the plate. This is accomplished by three washings with an anhydrous alcohol, either ethanol or isopropanol.

Many deep-etch plates are copperized today with a copperizing solution, which chemically deposits a thin layer of copper in the image areas. This layer of copper forms a very ink-receptive base and also extends the life of a deep-etch plate considerably. The copperizing solution is mainly an alcohol solution of a copper salt with a small amount of acid. It is applied to the plate right after the final alcohol wash, which was used to remove the deep-etch solution. After the copperizing solution has done its work, it is in turn rinsed off with three alcohol washes. The plate is then dried down in preparation for the application of the deep-etch lacquer.

The deep-etch lacquer consists of a vinyl resin dissolved with a dye in an organic solvent. A small pool of lacquer is applied to the plate and then spread over the entire surface. The plate is then dried down with a fan. This lacquer provides a chemically resistant, ink-attractive base for the image areas.

After application of the lacquer, some shops apply a litho asphaltum solution to further increase ink receptivity and to make washing out easier when the plate must be stored for any length of time. This solution mainly consists of gilsonite and an ink base in an organic solvent. When the asphaltum has been thoroughly dried down, developing ink is applied. This ink is usually a carbon black-pigmented litho varnish in petroleum solvents, which further increases the ink receptivity of the plate.

After the ink has been fan-dried, the plate is brought to the sink for removal of the stencil, which is the light-hardened coating in the nonimage areas. The plate is either placed under warm running water or in a trough of warm water for a few minutes. The stencil can then be removed by scrubbing the plate with a brush.

The plate is now given a final etch and gumming, just like a surface plate, so that the nonimage areas will repel ink and accept water. Many shops also apply a combination wash-out and asphaltum solution after gumming. This makes washing out easier if the plate is to be stored for any length of time. The plate is now ready for press.

The pollutants contributed by the deep-etch process fall into three general categories:

1. Toxic metals,
2. Acids,
3. Certain organic compounds.

Metals present in solution would be hexavalent chromium, iron, zinc, calcium, copper, and magnesium. Copper, iron, and chromium in sufficient concentrations are toxic to bacteria in secondary treatment plants. As mentioned previously, hexavalent chromium may be reduced to trivalent chromium with ferrous sulfate or sodium bisulfite in an acid medium. Then, upon addition of caustic soda or lime, the heavy metals will precipitate out as hydroxides.

The acids present include hydrochloric acid, which is usually present in copperizing solutions; certain organic acids, which come from the developer and etch; and the acid used in counteretching, which could be phosphoric, acetic, sulfuric, hydrochloric, etc. All of these acids can be neutralized by the addition of an alkaline substance such as caustic soda or lime.

The organic wastes consist of gum arabic, vinly resin from the lacquer, ink, alcohol, and solvents from the asphaltum solution and lacquer, etc. The biggest solvent problem in terms of volume is the alcohol, which is used in washing the plate and is also contained in the copperizing solution. It would be useful if the alcohol could be kept separate from the other waste by separate drainage into its own holding tank. A lot of the other organic waste might be filtered out with the aid of ferrous sulfate, which acts as a coagulant and thus is a good filter aid for suspended organic and inorganic matter.

The next type of plate to consider is the hard metal plate, which is used for exceptionally long runs. These plates consist of two or three layers of different metals so that, after processing, the image areas are resting on one metal while the nonimage areas are covered with a different metal. These plates can be either positive- or negative-working.

A bimetal plate consists of a base of aluminum, aluminum laminate, or stainless steel, which has been plated with a layer of copper. It is first counteretched, coated with deep-etch coating, and then exposed through a negative. The plate is developed with deep-etch developer, which removes the unexposed coating from the nonimage areas. A copper etch is applied, which removes the copper from the nonimage areas but does not touch the chrome. The etch is then flushed from the plate with water, and the hardened stencil is removed with the aid of an activator solution. The plate is flushed again, fresh activator is applied, and the plate is inked up with rub-up ink. After inking, the plate is flushed again to remove excess ink and is finished with gum and asphaltum.

Trimetal plates usually consist of chromium electroplated on top of copper, which has been plated on a base of mild steel, aluminum, or aluminum laminate. Such plates are positive-working and are processed much like deep-etch plates. During the etching step, though, a chromium etch dissolves the chromium away in the image areas, leaving the copper exposed. Then the stencil is removed with the help of an activator solution, and the plate is finished up like the bimetal plate described earlier.

Since many of the chemicals used to process a hard metal are used in deep-etch work, the waste products are similar. The only different chemicals used are the etches and the activating solutions. The copper etches for bimetal plates often contain either ferric chloride or ferric nitrate, some other metallic salts, and sometimes an acid. The chromium etch used for trimetal plates usually consists of a concentrated solution of metallic salts, such as calcium chloride, together with hydrochloric acid. The activator solutions generally contain sulfuric acid, some solvents, and a fatty acid.

The wipe-on plates are simpler to develop and process than any of the previous ones. Not only are they easily processed by hand, but they also can be run through a processor, which performs all of the steps automatically. The plate is usually anodized aluminum.

The first step in making a wipe-on plate is to apply a light-sensitive diazo coating. A typical diazo compound consists of the condensation product of formaldehyde and para-diazodiphenylamine. This powder is dissolved in a mixture of about 80 percent water and 20 percent methanol. Most of this coating adheres to the plate so there is not much pollution of water involved. Some chemicals will go down the drain, if the applicator sponge is rinsed in the sink.

After the diazo coating has been fan-dried, the plate is exposed through a negative. The plate is developed and the image lacquered in one step with a lacquer developer. A typical lacquer developer is a pigmented, two-phase emulsion, one phase being an aqueous gum arabic (or gum substitute) solution and the other being a polymer dissolved in an organic solvent. The aqueous phase develops the nonimage areas while the lacquer phase makes the light-hardened image areas ink receptive. Only 2 to 3 ounces of lacquer developer are used on a 40-by-48-inch plate. The plate is rinsed with water, and the excess water is squeegeed off. The plate is then gummed up with 8° Baume gum arabic or a specialty finisher. If the plate is processed through a processor, waste collection is simplified. The discharge unit can be hooked directly to a holding tank. Wastes from this process would include diazo and alcohol from the coating. The lacquer developer would contribute gum arabic or gum substitute, pigment, filler, organic solvent, resin, and some acid.

Presensitized plates I will only touch on very briefly. Many different ones are on the market today, so it is hard to be specific about what chemicals are involved. All presensitized plates, of course, are coated with special light-sensitive materials, and they can be either positive- or negative-working. The developers vary with the plate they are intended for; some are water-base, some contain solvents. The waste problem thus depends on just whose plate you are using.

But no matter what process a plant is using, it is plain that the waste products from platemaking cannot be ignored. My company and, I am sure, many other companies are busy trying to come up with new, less toxic chemicals to replace those now in use in some of our products. We also offer our customers advice on how to comply with their areas' sewage laws, and we point out which sections apply to them when using our chemicals. We also give them advice on how they can treat their wastes. Pretreatment of wastes by printing shops will go a long way toward easing the burden of municipal water treatment plants.

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DISCUSSION

MR. ROBERT L. KING (Environmental Protection Agency, Denver, Colorado): Have you done any water balance studies on the amount of water used for these rinseoffs?

MR. LATUS: No, we have not.

CURRENT STATUS OF WEB HEATSET EMISSION CONTROL TECHNOLOGY

Joseph L. Zborovsky*

Abstract

The industry has tried many control methods to comply with Federal, State, and local air pollution regulations. This report outlines all known methods that were used or showed promise through the first half of 1975. Information is provided to identify the advantages and disadvantages of each method. Recommendations are also made to evaluate the costs of investing in the various control devices.

INTRODUCTION

The desire of every printer using heatset inks (web offset or letterpress) is for a pollution-free ink equivalent in price and performance to conventional heatset inks, one which allows him to continue operations without making any additions or changes in the present hardware. Thus for the printer, the least burdensome solution to his problem is ink reformulation.

Extensive research by ink manufacturers has shown progress in this direction; however, no heatset ink formulation (or reformulation) will meet all regulations in every part of every State. Several formulations have been developed through substitution of ink vehicles (solvent) and reduction of their quantity. Experience with reformulated inks (ref. 1) has shown that some reduction is achieved in smoke, odor, and the total quantity of hydrocarbons emitted (table 1).

Low-temperature drying inks with "exempt" (photochemically unreactive as defined in Los Angeles Rule 66) solvents usually cost 50 percent more but use only 60 percent of the heat required for conventional heatset inks and produce less odor. However, when tested under operating conditions, low-temperature drying inks produced more smoke.

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*Environmental engineer, Graphic Arts Technical Foundation, Pittsburgh, Pennsylvania.

Table 1. Web offset inks for emission control

Ink Type	Percent solvent	Relative cost	Web temp. (°F)	Relative gas usage	Plume opacity (percent)	Relative odor
Heatset	40-45	100	300	100	15-20	100
Low-smoke	40-45	105	300	100	10-15	60
Low-solvent	25-30	120	270	85	5-10	40
Low-temp. dry[a*]	45-50	150	210	60	10-25	35
Low-temp. dry[b*]	25-30	125	230-250	60	15-20	slight
Low-temp. dry[c*]	25-30	105-110	220-250	87	none	slight
Heat-reactive	0-15	140-200	340	115	0-5	20
UV cure	0	200-300	120	0	0	trace

*a = ref. 1; b = ref. 2; c = ref. 3.

Low-solvent inks, e.g., 25-30 percent, appear to be the system that best satisfies the printer's needs, although the price generally runs 20 percent more than for conventional inks. The heat required is 15 percent less, and smoke and odor are significantly lower. Modification of dryer operation can further enhance this picture. Many printers have been using low-solvent inks where only smoke and odor regulations exist and the solvent is not photochemically reactive. Others have employed low-solvent inks as a temporary measure until a more permanent means of control is installed or available.

Attempts to reduce visible emissions by substituting different vehicles yielded no significant reduction in smoke. The heating requirements remain unchanged compared to conventional heatset inks. The price of the reformulated ink was 5 percent greater.

One novel approach to eliminating emissions from high-speed web operations is being used at Meredith Company (ref. 4). Instead of a heatset ink, an oxidative-drying ink is used, and a coating (a low concentration of a polymeric ester in ethanol and water) is applied and dried at 140°-150° F. The coating acts as a protective film to avoid setoff while the ink film dries underneath at its normal rate. No ink oil is emitted, as is the case in a conventional heatset ink, and the opportunity for visible emission and nuisance odor is virtually eliminated. The alcohol in the coating is recoverable and recyclable. Costs vary widely, depending on whether cover stocks or an entire magazine are printed this way. However, ultimate potential savings would include savings from paper as well as from drying operations.

The above control methods are the least burdensome for the printer, even though some changes in operating procedures and/or additional costs are involved. Unfortunately, however, more stringent control is necessary in some areas of the country, and more sophisticated, expensive, and extensive measures are required. These more extensive methods--unconventional or innovative inks and control equipment with conventional inks--are summarized in figure 1 and discussed in the sections that follow.

CONTROL TECHNOLOGIES

Heat-reactive Inks

Because the printer desires to maintain his present drying system, ink manufacturers investigated inks with different heat-drying mechanisms. Thermally catalyzed (heat-reactive) inks, an entirely different system chemically, require a 15 percent increase in gas and cost 40 to 100 percent more. However, a noticeable emission reduction was observed when the inks were submitted to analysis

UV Inks

Ink manufacturers have recognized the need for a new ink-drying process for many years. Although they realized the complexity of the printer's immediate demands, they decided to concentrate some of their efforts on the longer-term development of a pollution-free ink (no solvent, no emission) using a different process to dry the ink film. Today their research efforts have produced a commercial success with UV (photoreactive) inks.

UV ink systems meet all the emission regulations and produce good print quality. UV inks appear to be the pollution control method presently closest to the ideal. The high costs of ink and hardware are a major consideration, but in certain circumstances are economically feasible. If

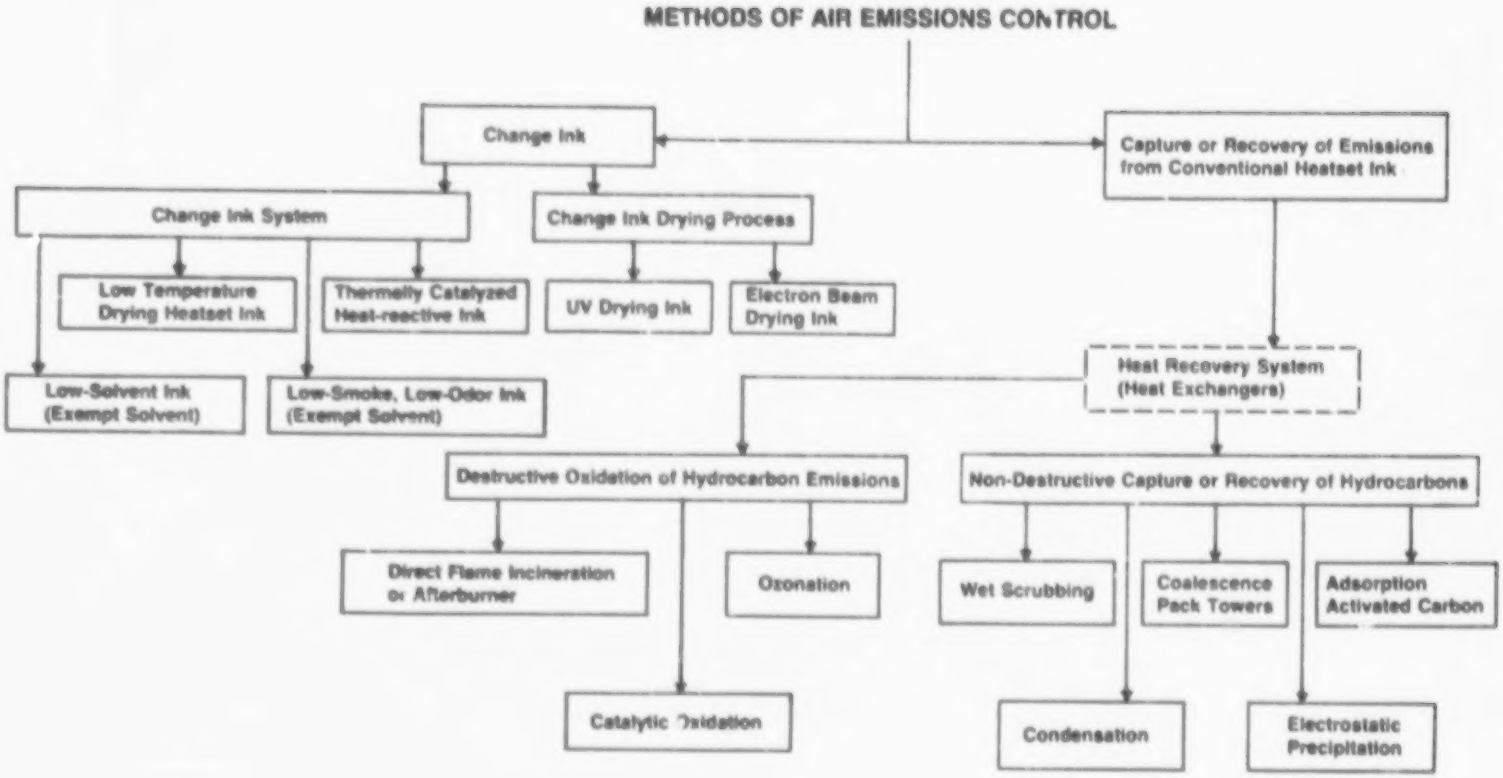
METHODS OF AIR EMISSIONS CONTROL
Change Ink
Capture or Recovery of Emissions from Conventional Heatset Ink
Change Ink System
Change Ink Drying Process
Low Temperature Drying Heatset Ink
Thermally Catalyzed Heat-reactive Ink
UV Drying Ink
Electron Beam Drying Ink
Low-Solvent Ink (Exempt Solvent)
Low-Smoke, Low-Odor Ink (Exempt Solvent)
Heat Recovery System (Heat Exchangers)
Destructive Oxidation of Hydrocarbon Emissions
Non-Destructive Capture or Recovery of Hydrocarbons
Direct Flame Incineration or Afterburner
Ozonation
Catalytic Oxidation
Wet Scrubbing
Coalescence Pack Towers
Adsorption Activated Carbon
Condensation
Electrostatic Precipitation

Figure 1. Pollution control techniques applicable to web offset.

costs can be justified and some performance problems eliminated, the UV system, considered revolutionary by some in the industry, may become a very widely used drying process.

Electron Beam Drying (EBD)

Electron beam drying is another of the new drying systems. Although it has not yet achieved commercial acceptance, this process has no pollution potential and can dry (cure) ink films which are too thick to be cured by UV. Tests are anticipated for both gravure and offset in 1975. This system may be most practical for screen printing (ref. 5). Some developers of EBD systems feel that its potential is fairly unlimited in all areas of printing.

Destructive Oxidation

Within the past 4 years thermal and catalytic oxidation of hydrocarbons has been used successfully to control emissions in the printing industry. Incineration techniques now available can control the emission of almost every known hydrocarbon by converting it into carbon dioxide and water (ref. 6). The various incineration processes differ only in reaction mechanisms and temperatures. Process designs differ primarily in control of temperature, turbulent mixing of gases, and kinetic reaction contact times (ref. 7).

Optimum operational design of equipment is extremely important in incineration processes. Insufficient temperature: nonhomogenous mixing of hydrocarbons, gas, and air: and/or insufficient time in the reaction zone contribute to incomplete combustion, which yields carbon and carbon monoxide. These unwanted reaction products can be generated in sufficient concentrations to cause smoke, hydrocarbons, and/or carbon monoxide to be emitted. Some companies, in a false economy move, reduce the fuel feed to the afterburner, leading to incomplete combustion, visible emissions, and citations.

A problem common to all combustion systems is the possibility of oxidizing atmospheric nitrogen at high temperatures into nitrogen oxides, which also are an air pollutant.

Direct flame incineration (afterburners): Many direct flame incineration processes differ only in the design of fuel burners, baffling, and constriction devices employed to optimize turbulent mixing of gases before combustion. Automatic fuel and air flow controls are available to maintain stoichiometric flow rates to achieve complete combustion. Incineration requires oxidation temperatures in the 1,100°-1,200° F range (ref. 8) and sufficient time in the reaction zone. Proper contact time is dependent upon the kinetic rate of reaction (oxidation) for that organic component in the effluent having the slowest reaction rate.

Within the past year, printers have been extremely cautious about installing afterburners because of fuel shortages. Fuel requirements for afterburners depend on the air-handling rates of press dryers. Theoretically, a typical afterburner for a press dryer operating at STP would use about 105 cfm of natural gas (100 percent methane) per 1,000 scfm of spent dryer gases. Based on September 1974 rates in Pittsburgh (ref. 9), the natural gas costs for this afterburner would be about 14 cents per 1,000 scfm of spent dryer gases.

Some printers using afterburners are now considering replacing them with other control devices requiring less energy. Over the last year, as many as 20 afterburners have been installed and equipped with heat exchangers that can reclaim as much as 40 to 60 percent of dryer and afterburner heat.

The prime advantages of direct flame incineration are essentially complete oxidation of all organics, no smoke or odor, moderately priced hardware, and minimum maintenance. The major disadvantage has become recently apparent with short fuel supplies and soaring costs. Current domestic production of natural gas is predicted to be 75 percent lower by 1985 with prices increasing twofold to fourfold (ref. 1). Economists have been projecting shortages in domestic supply and imports of expensive liquid natural gas--unless industry reduces consumption, new gas reserves are found, and/or synthetic gas processes are developed. Gas suppliers have already reduced allocations to some companies by 15 to 60 percent while others require 1- to 2-year waiting periods for either new customers or for increased allocation.

The use of regenerative heat exchangers may recover as much as 70 percent of the waste heat, but the severity of temperature and ink solvents, resins, dust, etc., all detract from the life and performance of this type heat exchanger (ref. 11). The use of heat exchangers and/or the replacement of inefficient gas dryers, however, can save as much as a 76 percent (ref. 12) in natural gas costs.

Given unlimited fuel supplies, the overall air quality performance of direct flame incineration would have to be rated as excellent.

Catalytic oxidation processes: Like direct flame incinerators, the catalytic oxidizer also converts hydrocarbons into carbon dioxide and water but uses a different reaction mechanism and at a lower reaction temperature (ref. 13). The oxidation rate accelerates in the presence of an appropriate catalyst, and the temperature required is lower, the optimum depending upon the catalyst used. Reports have been made that optimum hydrocarbon oxidation could be accomplished at reaction temperatures as low as 650°-700° F (ref. 14).

Typical catalysts are the transition metals or their oxides: iron, cobalt, nickel, platinum, palladium, copper, and silver. Catalysts are usually manufactured by coating an inert support material with a finely divided metal or metal oxide. The catalyst usually used in the industry is a platinum and/or palladium coating on a ceramic cylindrical pellet. The catalyst bed is usually located in a temperature-controlled heating zone where premixed stoichiometric quantities of atmospheric oxygen, fuel, and hydrocarbon (organics) react to form carbon dioxide and water. Control of temperatures and contact time with the catalyst bed are especially important to insure complete oxidation.

Improper temperature or contact time can cause incomplete oxidation, yielding carbon, carbon monoxide, and side reactions such as resin polymerization. Polymerized resins condensed on the catalyst surface can deactivate the catalyst or plug the catalyst bed.

Catalysts are susceptible to substances that inhibit or destroy (poison) their activity, even in minute amounts or very low concentrations. Certain heavy metals, halogenated hydrocarbons, and organosilicon compounds in trace quantities will poison many catalysts. In practice, catalyst cost, life, physical strength, resistance to thermal shock, and resistance to poisoning are factors that must be considered in addition to activity and specificity. All catalysts are expensive, especially those using precious metals: platinum, palladium, and silver. In considering a catalyzed system, evaluations of catalyst replacement or regeneration must be made.

A distinct advantage of this process is that less natural gas is consumed than in the direct-flame afterburner incinerators because of the lower reaction temperatures. However, catalytic systems can waste fuel and energy, just as the afterburner, unless heat recovery is employed with heat exchangers.

Ozonation: Ozonators produce ozone by applying a high voltage alternating current to an air space between two insulated electrodes. Permeating the air space is a charge which converts atmospheric oxygen to ozone. The spent dryer gases are mixed with the ozone, creating oxidation products frequently soluble in water or in a slightly basic, aqueous solution. Ozone generators produce 0.1 pounds of ozone per kilowatt hour of electricity consumed.

Ozonators have been equipped with catalysis beds and with wet scrubbers to optimize oxidation and to remove water-soluble carboxylated hydrocarbons from the stack effluent (ref. 15). But the use of afterburners with ozonators cannot reduce afterburner gas consumption significantly because reaction temperatures must be maintained at 1,100° to 1,200° F (ref. 8) to oxidize all those molecular sites not oxidized by the ozone

The major use of an ozonator is only to oxidize the most odorous hydrocarbons into a less objectionable form, though without any change in the rate of hydrocarbon emissions (pounds of carbon per hour). The process has not gained wide acceptance because ozone reacts very slowly or not at all with saturated hydrocarbons. (Ozone readily oxidizes unsaturated hydrocarbons.) Ozonators have been used successfully with other incineration processes to speed up oxidative reactions. Pilot tests in our industry, however, indicate that ozonation will not effectively eliminate odorous emissions from web dryers (ref. 13).

Nondestructive Control Processes

Petroleum derivatives make up about 80 percent of conventional heatset inks (55 percent solvent). Last year, the price of ink solvents increased by 340 percent (ref. 16). This year, ink vehicles are expected to increase in price an average of 25 percent. No relief is foreseen from these spiraling costs (ref. 17).

Clearly, incineration destroys a prime raw material--one expected to continue to increase in value into the foreseeable future. Even in incinerators equipped with heat exchangers, the market value of the solvent lost exceeds the market value of the heat recovered. (Ninety-five gallons of solvent is equivalent in heating value to about 0.5 tons of coal or 10,000 cubic feet of natural gas. See table 2.)

Nondestructive recovery control devices may not only offer an acceptable means of emissions control, but also help conserve these ever more-expensive petroleum derivatives. Ink solvents have been successfully recovered from these types of devices and substituted for No. 2 fuel oil in diesel engines and oil heaters. Last year, recovered ink solvents were sold for 20 to 50 cents per gallon. The use of recovered solvents in ink manufacture, however, has not yet been proven successful.

Many nondestructive recovery control processes have been developed or are under development. As yet, most have had limited success in meeting

Table 2. Value of ink solvent loss in incineration

Fuels	Market price	Heat of combustion	Quantity to produce 1.1×10^7 Btu	Cost of equipment heat
Ink solvent	0.50/gal	11,250 Btu/lb	95 gal	47.50
Natural gas	$1.40/10^3 ft^3$	$1,100 Btu/ft^3$	$10^4 ft^3$	14.00
Propane	0.32/gal	91,500 Btu/gal	120 gal	38.40
No. 2 fuel oil	0.37/gal	140,000 Btu/gal	80 gal	29.60
Kerosene	0.385/gal	135,000 Btu/gal	81 gal	31.37
Coal (bituminous)	35.50/ton	13,000 Btu/lb	0.445 tons	15.60
Equivalent electrical energy	0.06/kWh	* 3,413 Btu/kWh	3223 kWh	193.34

*Heat conversion factor.

air quality standards and in recovering ink constituents. Even so, there can be little question that the philosophy behind the approach is fundamentally sound. Solvent emissions into the atmosphere should be viewed as a "misplaced resource," a resource to be conserved in a time of shortages and increasing prices.

Wet-scrubbing processes: Wet-scrubbing systems are used successfully in the chemical industry to clean and purify gas streams from manufacturing processes. Vapors are removed from the gas stream by a series of steps in which the stream is sufficiently cooled to condense and form microscopic colloidal particles. These particles enlarge through impingement on droplets of water or wetted surfaces. The liquified chemical particles either diffuse into the water droplets or agglomerate and become large enough to separate out of the gas stream by gravity.

Some wet scrubbers use only water or aqueous solutions of water-soluble organic chemicals or inorganic salts to improve efficiencies and insure dissolution or emulsification of the hydrocarbons into an aqueous phase. The aqueous scrubbing liquor readily absorbs heat from the spent dryer gases and saturates the air with water vapor (steam). Wet scrubbers that do not adequately precool spent dryer gases (such as those with a heat exchanger) produce a characteristic white steam plume, which eventually dissipates.

The disposal of the aqueous scrubbing liquor may be a problem because the dissolved water-soluble hydrocarbon or organic material will contribute to the pollutants in the aqueous effluent.

Aerosols' wet scrubber: The pollution control device manufactured by Aerosols Control Corporation (figure 2) is a combination of two basic processes where hydrocarbon vapors are scrubbed with an aqueous solution. A fiberglass filter bed backs up the system by coalescing liquid chemical particles that have not enlarged enough to separate from the gas stream by gravity.

The scrubbing liquor contains sodium hydroxide and dioctylphtalate (DOP) to dissolve and emulsify the hydrocarbon vapors, and surfactants to prevent the buildup of foam in the system. A sump tank containing 100 to 150 gallons of the scrubbing liquor traps about 8 pounds of emulsified hydrocarbons per hour. The liquor is dumped and replenished weekly.

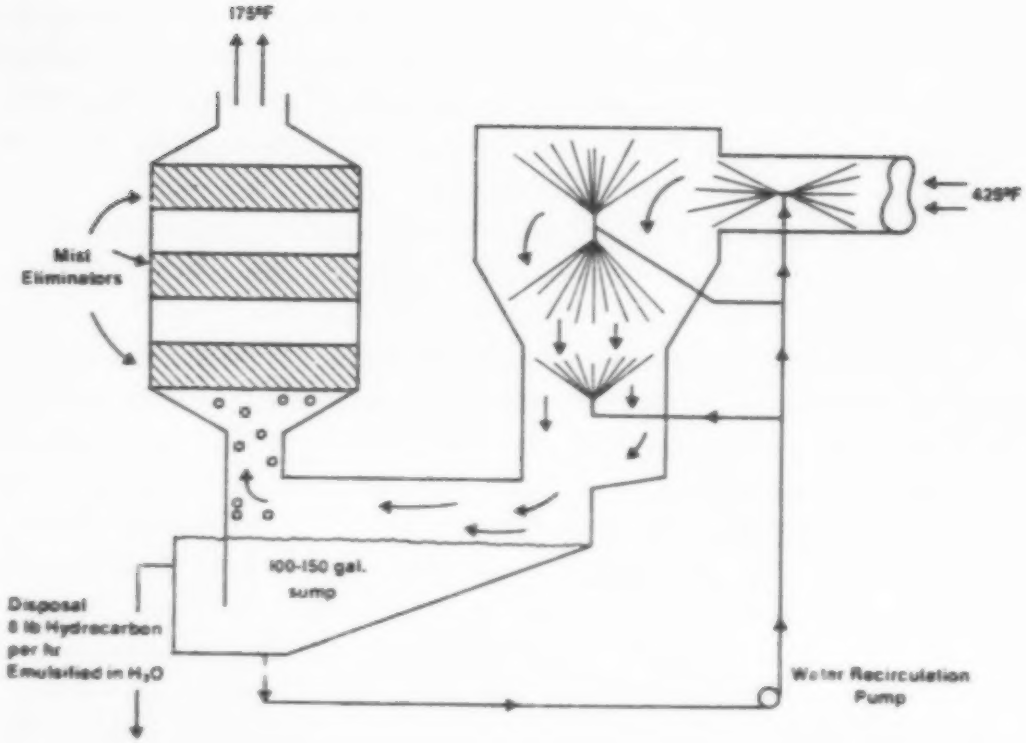
175°F
Mist Eliminators
429°F
100-150 gal. sump
Disposal 8 lb Hydrocarbon per hr Emulsified in H_2O
Water Recirculation Pump

Figure 2. Aerosols Control Corporation web scrubber.

When this unit was in operation in the industry, it processed 2,500 scfm of exhaust gases from a Ross combination dryer on a M-1000 web offset press.

The manufacturer claims the unit can remove as much as 99 percent of the hydrocarbon emissions and reduce the visible emissions to 0-5 percent opacity. A State air inspector reported that, although the total hydrocarbon emission was held below the 0.8 lb/hr State requirement, the maximum efficiency of the Aerosols scrubber was only 83 percent. The manufacturer also reports a normal 90 percent efficiency with normal ink coverage. If isopropanol is present in the fountain solution, the efficiency drops to 87 percent.

The State inspector said the scrubber permits as much as 30 percent visible emissions and does not meet the State requirement of 0 percent opacity. Operational problems could cause this discrepancy. The inspector suggested that adequate precooling would normally control visible emissions. We believe a heat exchanger before the scrubbing unit would meet this need.

But because the Aerosols wet scrubber was not complying with the local visible emissions standard, the printing plant where it was installed was pressured by the local regulatory agency to replace the Aerosols unit with a device such as an electrostatic precipitator (which is known to provide compliance only with the visible emissions standard).

The capital costs and installation costs of the Aerosols unit are comparable with incineration. The only "real savings," perhaps, lies in lower operational costs in water consumption, chemicals in the scrubbing liquor. and the use of electrical energy as opposed to natural gas.

CVM Fume Eliminator: The Fume Eliminator manufactured by the CVM Corporation (figure 3) does not significantly differ in principle from the

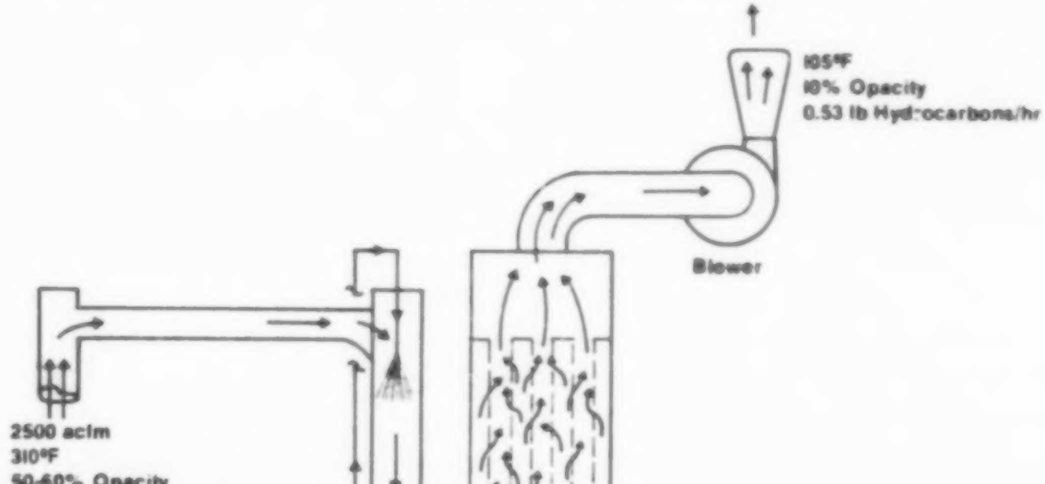
105°F
10% Opacity
0.53 lb Hydrocarbons/hr
Blower
2500 acfm
310°F
50-60% Opacity
3.15 lb Hydrocarbons/hr
Oil Layer
Aqueous Layer
2.62 lb Hydrocarbons/hr

Figure 3. CVM Corporation fume eliminator.

Aerosols wet scrubber but shows significant differences in hardware design and power requirements. The system is equipped with a water scrubber tower that cools the hydrocarbon vapors to below their boiling point to facilitate the enlargement of colloidal droplets. Suspended droplets are passed through a bed of fine fibrous material (fiber glass wool) sandwiched between supporting grids. As the droplets pass through the fibrous bed, they coalesce by the impingement of larger droplets and the bed packing. As the droplets grow larger, they collect on the bed packing and drain off into a sump for removal from the system. (There are no reports of the recovered ink solvents being sold. However, they have been used successfully and experimentally as a heating fuel oil.)

The power requirements of the exhaust blower and the water recycle pump are about 4 to 5 horsepower for every 1,000 cubic feet of spent dryer gas processed per minute.

Periodically, the fiber glass bed elements may require replacement. There is no reported evidence of element fouling if used in continuous service for 6 months. Expected element life can exceed a year with a minimum service of 18 turns per week. Element replacement cost and labor would be about $400 per 1,000 scfm capacity.

The manufacturer claims 83 percent removal of hydrocarbons, and the opacity of the plume has been consistently less than 10 percent. The State air quality inspector quoted earlier reports that with medium to heavy ink coverages, the CVM device will reduce emissions by 83 percent and occasionally perform in compliance (85 percent). According to him, visible emission (20 to 5 percent opacity) is the only serious problem and appears to be attributable to inadequate cooling in the first stage of the unit.

The plant in which the CVM unit was installed has since terminated the unit's operation. Consideration was given to transferring the device to a plant in another State within the corporation. After extensive studies comparing its performance with other pollution control devices, it was decided that the CVM unit could not provide compliance with either the hydrocarbon or visible emissions regulations.

Elbair wet scrubber. The Elbair wet scrubber (figure 4), marketed by Peninsula Lithograph Company (PenLitho), is a simple water-scrubbing system in which the spent dryer gases pass horizontally through two high-pressure

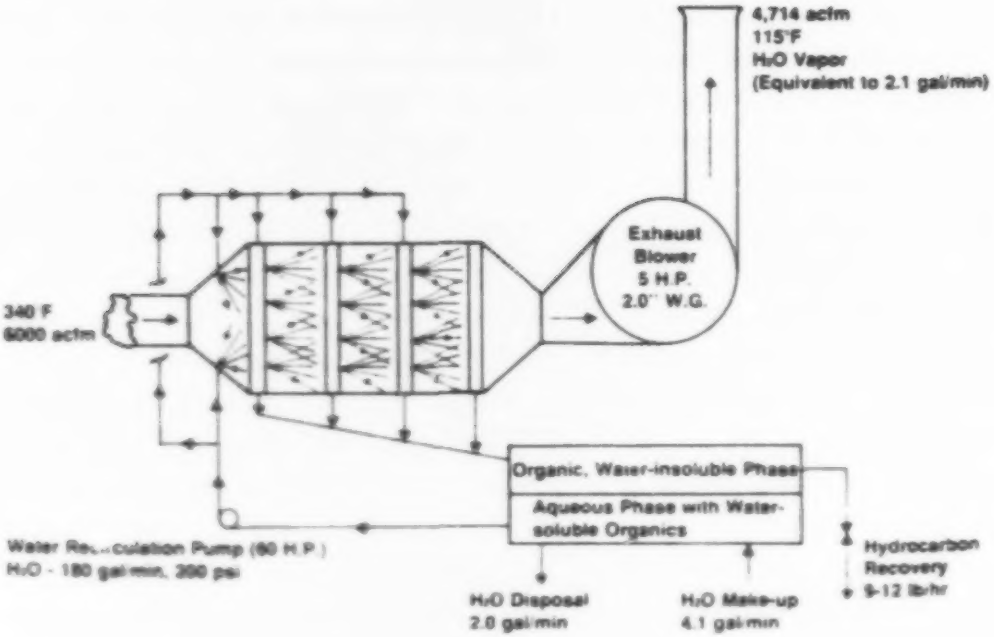
4,714 acfm
115°F
H_2O Vapor
(Equivalent to 2.1 gal/min)
Exhaust
Blower
5 H.P.
2.0" W.G.
340°F
6000 acfm
Organic, Water-insoluble Phase
Aqueous Phase with Water-soluble Organics
Water Recirculation Pump (60 H.P.)
H_2O - 180 gal/min, 200 psi
Hydrocarbon
Recovery
9-12 lb/hr
H_2O Disposal
2.0 gal/min
H_2O Make-up
4.1 gal/min

Figure 4. Elbair wet scrubber (Peninsula Lithograph Co.).

jet streams of water that precool the vapors. The precooled vapors condense and then pass through a series of three horizontal, 10-gallon housings, each of which is equipped with four high-pressure spray nozzles. The spray nozzles are directed to patented vertical impinging plates. The recovered ink solvent and scrubbing water liquor is collected from a drain in each housing and transported to a phase separation tank. The aqueous phase is recycled and the water-soluble ink solvent periodically drawn off.

The Elbair wet scrubber has been accepted by the San Francisco Bay Area Air Pollution Control Agency. PenLitho claims their scrubber recovers as much as 95 percent of the hydrocarbon emissions. Although a white steam plume is always visible, the plume opacity (5 to 15 percent) is acceptable to the regulatory agency.

The maximum energy requirement for this system is 65 horsepower for the exhaust blower and the water spray pump.

PenLitho claims they can operate this pollution control device for only 50 cents an hour and recover 1.5 gallons of ink solvent per hour for resale. They claim that they will pay off this scrubber in only 22 months.

The only disadvantage we could perceive is the heat losses that might be salvaged with heat exchangers. The evaporation rate of water lost (2.1 gal/min) alone accounts for a heat loss of 17,900 Btu per minute which is equivalent to heat from 978 cubic feet of natural gas per hour ($1.39/hr).

To our knowledge, there are only two printers using the Elbair wet scrubber to control hydrocarbon emissions. One of the two replaced afterburners with the Elbair unit because of reduced natural gas allocation in the area. Using limited gas supplies for incineration became a luxury the company could not afford.

Electrostatic precipitation. United Air Specialists, Inc., has been manufacturing an electrostatic precipitation control device called a "Smog-Hog" (figure 5). The "Smog-Hog" is a rather simple operating system. A heat exchanger or heat wheel is used to cool and condense spent dryer gases into liquid droplets. The airborne droplets then pass through an electro-

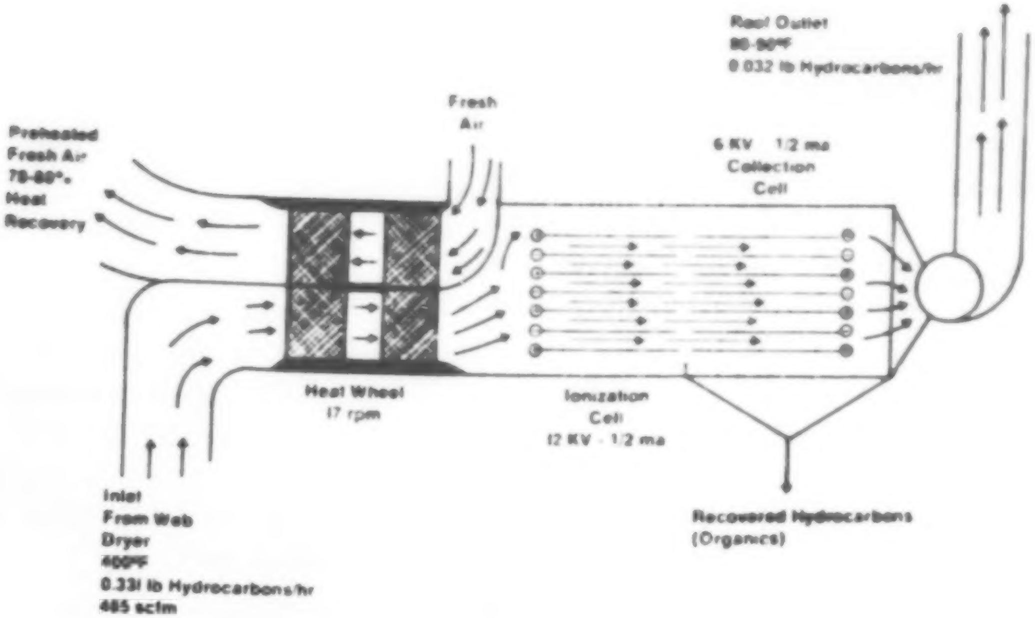
Roof Outlet
80-90°F
0.032 lb Hydrocarbons/hr
Fresh Air
Preheated Fresh Air 70-80°, Heat Recovery
6 KV 1/2 ma Collection Cell
Heat Wheel 17 rpm
Ionization Cell 12 KV - 1/2 ma
Inlet From Web Dryer
400°F
0.331 lb Hydrocarbons/hr
485 scfm
Recovered Hydrocarbons (Organics)

Figure 5. United Air Specialists "Smog Hog."

static ionizing cell that places an electric charge on each droplet. The charged droplets are then collected in the next electrostatic cell where the droplets agglomerate on the vertical cell plates, draining off by gravity.

The manufacturer claims at least an 85 percent removal of all hydrocarbon emissions with no smoke and odor.

No evidence has come to light refuting the recovery efficiency of the "Smog-Hog." Reports of many observers indicate no visible emissions and only slight traces of odor.

The only electrical power demands are for the motor drive of the heat wheel, electrostatic cells, and the exhaust blower. The precipitation power is only 20 to 50 watts per 1,000 cfm of exhaust.

The manufacturer claims operating costs rarely exceed 0.1 cent per 1,000 cfm. They also claim that the heat wheel recovers 70 to 80 percent of the heat loss. According to reports, no printer has taken advantage of this recovered heat.

The Betran electrostatic precipitator differs from the UAS "Smop-Hog" only in design, and eliminates visible emissions equally well. However, in a recent GATF performance study during a Beltran pilot test, this device demonstrated that the hydrocarbon emissions were not significantly reduced. Its major performance problems appear to be temperature control of the incoming gases and the residence time in the electrostatic cell. Thus, its application for compliance appears limited to areas where high reductions in organic emissions are not required.

Activated carbon adsorption: The power of activated charcoal to remove or adsorb many different hydrocarbon gases, vapors, and odors has been known for over 100 years. The adsorbing power of activated charcoal differs for each adsorbate and depends on the physical and chemical properties of the adsorbate.

The Los Angeles Lithograph Co., Inc. (L.A. Litho), is currently marketing a patented activated-carbon pollution control device (figure 6), which they have demonstrated at their plant as an efficient means of complying with the Los Angeles air quality standards.

In the L.A. Litho system, spent dryer gases pass through a manifold plenum, which evenly distributes the gas flow into three of the four

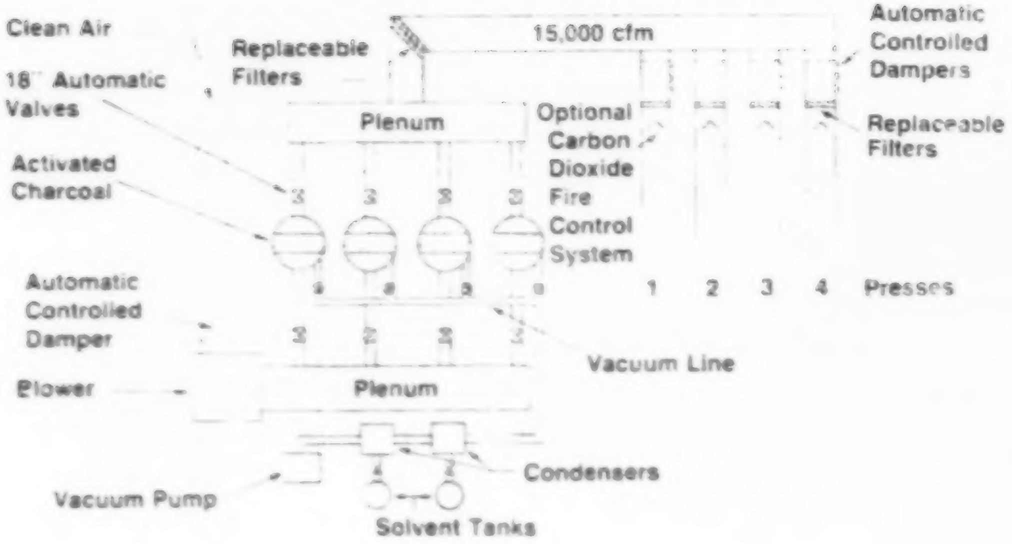
Clean Air
Replaceable Filters
15,000 cfm
Automatic Controlled Dampers
18" Automatic Valves
Plenum
Optional Carbon Dioxide Fire Control System
Replaceable Filters
Activated Charcoal
1
2
3
4
Presses
Automatic Controlled Damper
Vacuum Line
Blower
Plenum
Condensers
Vacuum Pump
Solvent Tanks

Figure 6. L.A. Litho activated carbon adsorber.

activated charcoal beds. While three beds are adsorbing hydrocarbons, the fourth is being regenerated. It remains on automatic standby until one of the other three beds reaches its maximum loading capacity of adsorbed hydrocarbons.

During the regeneration cycle the adsorption bed is sealed off from the intake and exhaust manifolds. An electrical heating element in the bed heats the adsorbates on the charcoal, while a vacuum pump produces a vacuum of 1 Torr (1 mm Hg). This reduced pressure allows the adsorbed hydrocarbons to be flashed off at a temperature much lower than the boiling point of the hydrocarbons at atmospheric pressure. The distillate hydrocarbon is recovered, and the adsorption bed is reactivated. The hydrocarbon vapors condense in a water-cooled condenser and a refrigerated trap. The water-cooled condenser separates the high-boiling hydrocarbons (ink solvent), and the freeze trap recovers the low-boiling and low molecular weight hydrocarbons.

The regeneration process of the adsorption bed is unique because flash evaporation processes have not been developed commercially to desorb high-boiling hydrocarbons from activated charcoal. L.A. Litho reports hydrocarbon recoveries of 90 to 95 percent with no visible emissions and only very slight traces of odor.

The Los Angeles Air Pollution Control Department has monitored the emissions from L.A. Litho, and no objections have been reported.

The only electrical demand is the 75 horsepower blower and the 2-hours-per-day use of the regeneration equipment such as bed-heating element, vacuum pump, and the refrigeration unit. L.A. Litho claims that this system processes 15,000 scfm of spent dryer gas for less than 15 cents per hour. The estimated initial cost of this system is in the neighborhood of $7.00 per cfm.

The high-boiling hydrocarbon is recovered as a dark "tarry" liquid, which after suitable filtering may be used as a diesel fuel oil. Ink manufacturers attempted unsuccessfully to utilize this recovered solvent as an ink vehicle or press wash-up solvent. Last year, L.A. Litho marketed the recovered hydrocarbon as a fuel oil. (However, during the oil embargo they discovered they could use this oil more economically in their own diesel trucks!)

Although this activated charcoal adsorption process appears to be a viable system to combat hydrocarbon, smoke, and odor emissions, L.A. Litho has been troubled with many operational and equipment malfunctions. A redesign of hardware and addition of adequate process control devices may be necessary to eliminate the temperature and pressure control problems encountered.

DISCUSSION

Equipment Costs

Estimates of the initial costs of pollution control hardware are difficult to correlate because prices vary with the size of the unit, volume of air-handling capacity, and the date of the price quote. The estimates presented in table 3 do not include the cost of installation.

Operating expenses include the consumption of gas, water, and electrical utilities; and these have been calculated from a common rate for all three utilities. The operating expenses of labor and replacement parts are unavailable.

The table also designates the major source of energy (natural gas or electricity) for each process. The processes that recover potentially saleable hydrocarbons and the processes which may present a water pollution problem also are indicated.

Table 3. Comparison of pollution control processes

	TEC Afterburners								
	A[1]	B[2]	Incinerator	Catalytic	Aerosol	Pen-Litho	CVM	L.A. Litho	UAS
Costs:									
Hardware ($/cfm)	6-13	8-18	3-6	3-8	5	4-7	4	7-10	4-6
Operation ($/Mcfm)			2.42	0.53	1.20	0.001	0.001	0.01	0.001
Major energy consumed:									
Natural gas	x	x	x	x					
Electricity					x	x	x	x	x
Systems with:									
H_2O disposal					x	x	x		
Recovery of hydrocarbon						x	x	x	x

[1] With 40 percent heat recovery.

[2] With 60 percent heat recovery.

Performance and Compliance

With the exception of afterburner incinerators, most newly installed pollution control devices have had some difficulty being totally accepted by the local regulatory agencies. Regulatory agencies have been cautious in accepting any unproven control device that might establish a precedent.

Recovery of Heat Losses

The use of heat exchangers to cool spent dryer gases will improve recovery efficiencies of all pollution control devices with the exception of the UV and electron beam systems. Fuel reduction can also be accomplished with these systems to reduce the operating costs of gas dryers and afterburner incinerators.

The use of afterburners, even with heat exchangers, does not appear to be an economical means to control emissions. Afterburners incinerate $47.50 worth of ink solvent to produce the same quantity of heat as $14 worth of natural gas.

The value of natural gas saved through heat exchangers and the resale value of recovered ink solvent suggest that each printer should consider some of the advantages of recovering heat and/or ink solvents to help meet future needs.

New Ink Systems

The UV inks and drying systems appear to be one of the most promising methods of eliminating hydrocarbon emissions. The deterrent for most printers is absorbing the high costs of ink and hardware. The low-smoke, low-solvent, and low-temperature drying inks show some reduction in emissions and fuel consumption; however, all show some increase in cost over conventional heatset inks.

Recommended Approach to Pollution Control

Before a printer invests in a method of pollution control, he must evaluate the immediate and long-range economic factors that will affect the initial capital outlay, operational overhead, and the advantages of payback features.

When considering the various alternative control methods, the effects of inflation on the cost of equipment and the cost of labor to install that equipment may make it necessary to determine a time-price relationship.

Overhead expenses must also be approached with caution. Energy, manpower, raw material consumption, and parts replacement must all be given equal weight. The printer will have to ask himself some critical questions. Will the addition of this control technique reduce or add to present overhead costs? Can the printer withstand possible reductions in future fuel allocations and increased costs of natural gas and critical raw materials?

The printer must consider whether heat and hydrocarbon recovery have real payback features. With the high cost and the availability of natural gas and petrochemicals such critical factors, loss of heat and ink solvents must be considered as "misplaced resources."

In many regions of the country there are tax incentives available where pollution control equipment must be installed. The printer should investigate this. Some offer exemptions from sales taxes, others increased rates of depreciation or other "tax-breaks" on new control equipment. The cost of pollution control is, of course, passed on to the consumer ultimately.

Some companies in other industries have investigated all the above economic factors associated with pollution control and discovered that besides complying with the air quality regulations, the control equipment can offer a reduction of energy requirements, a "tax break," and an eventual payoff of the investment with a recovered, saleable product.

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NOTE. - A joint discussion with Zborovsky and Fremgen follows Fremgen's paper.

MONITORING AND TESTING OF EFFLUENTS FROM LETTERPRESS AND OFFSET PRINTING OPERATIONS

Robert D. Fremgen*

Abstract

The methods of investigation and quantitative results obtained in monitoring and testing emission control equipment are described. Introductory background includes the mechanisms and methods of drying as well as the materials employed that give rise to hydrocarbon emissions. A number of isokinetic source tests were made in conjunction with the evaluation of electrostatic precipitators and fiber bed collectors. Evaluations in both letterpress and web offset operations are reported. Simultaneous source testing of input and output streams is covered along with the particulars of the modified EPA impingement train used for source testing. The results include the correlation of analytical testing with the actual recovery of hydrocarbon oils from control devices as well as the performance of emission control equipment.

INTRODUCTION

In determining hydrocarbon emissions from web printing operations there are three principal interrelated systems elements that affect the result. These are: the printing operation, the source sampling and analytical techniques, and the emission control equipment if such exists.

With regard to the printing system, this investigation encompasses web printing both by the letterpress and offset methods. Heatset inks are employed extensively with both of these processes. Compositions will vary considerably to accommodate either method as well as multitudinous product possibilities. Briefly, heatset inks derive their name from the inherent physical characteristics of the resinous binders used in these compositions. Apparent dryness is achieved by two mechanisms in successive stages of the drying process. In the initial phase of drying, temperature and air velocity are used to partially evaporate the solvent. In the second stage of the process, the ink film is chilled to congeal and harden the high-melting-point resinous components. These two operations convert the ink film to a quasi nontacky and unsmearable condition.

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*Chemical Process Engineer, Research and Development Department, Dayton Press, Inc. (formerly the McCall Printing Co.), Dayton, Ohio.

The high-boiling oils employed in heatset inks serve both as a solvent for the resinous binders and as a carrier of color matter to the imprinted image. These ink oils are the primary source of hydrocarbons which occur as emissions from web printing operations.

While ink oil is seemingly a common denominator, these oils are a broad and complex category of hydrocarbon materials. In general, the individual oils are selected petroleum fractions in the higher boiling range of derivatives akin to kerosene and the fuel oils. There are in use a series of a dozen or more narrow- to broad-cut fractions having their boiling point range anywhere from 400° to 700° F. One or more of these oils are used in proportions suited to meet specific product and process requirements; these include, for example, the nature of the substrate to be printed, the method of printing, drying conditions, and the like.

Being mixed species, the ink oils are compositionally identified only in a very general sense. For the most part, the ink oils are composed of mixed paraffins of the normal and isoparaffinic variety together with the presence of cycloparaffins in some instances as well. They usually also contain some aromatic and olefinic hydrocarbons, thus being within but generally not too far removed from the usual regulatory definition for photochemically reactive material. Consequently, deodorized grades of some ink oils are now available which are outside this photochemical definition. More recently, further refined grades of some ink oils have been commercialized; these are comprised of fully saturated hydrocarbons. These two newer varieties of the ink oils have achieved some degree of popularity. Yet, their photochemical activity is only generally classified by virtue of extrapolation from that which is known of their chemical characteristics; substantially less is known of the emission products therefrom.

The drying operation is quite pertinent, since this is where emissions are generated. In web printing heat is transposed to the moving sheet in a variety of ways. These include conduction, convection, and radiation;

in more than a few instances drying systems include combinations of these. Such heating is accomplished by hot air streams, steam drums, direct flame impingement or various combinations thereof.

Most dryers make use of moderate- to high-velocity hot air, as depicted schematically in figure 1. Invariably, heatset printing will include the chill roll stand where the web is cooled to harden the ink film thereon. While the temperature of the drying air may reach as high as 550° F or more. web temperatures of 275° to 350° F are quite common. Since web speeds range from 800 to 1,800 feet per minute, this heating is usually accomplished in a time span of one-half to one second. Within this short interval, a portion of the ink oil is vaporized, partially recirculated within the hot air plenum, and partially exhausted.

Conceptually web printing is regarded as a continuous process. This generalization, however, is somewhat deceiving. More accurately, web printing is a random series of time-spaced continuous cycles. For example, a typical time-temperature chart from a dryer recorder (figure 2) shows running increments of various durations. Moreover, the idle cycles here shown exclude the "make ready" period when a particular job is set up on the press.

This random sequence condition shows that more than casual care is required to assure that source tests are run at equilibrium conditions of the systems at hand. Beyond the test operation, however, emission rates are quite another question Process and job variations preclude an absolute rate. Emissions are best expressed in terms of their concentration and the rate per hour. The expression of emissions for web printing as a daily rate has little meaning.

METHODS OF SOURCE TESTING AND ANALYSIS

A modification (ref. 1) of the EPA Method 5 impingement train was employed for source testing. The equipment configuration (figure 3) is somewhat different than that used for particulate sampling.

In brief, with this modification the sample probe is not heated. The

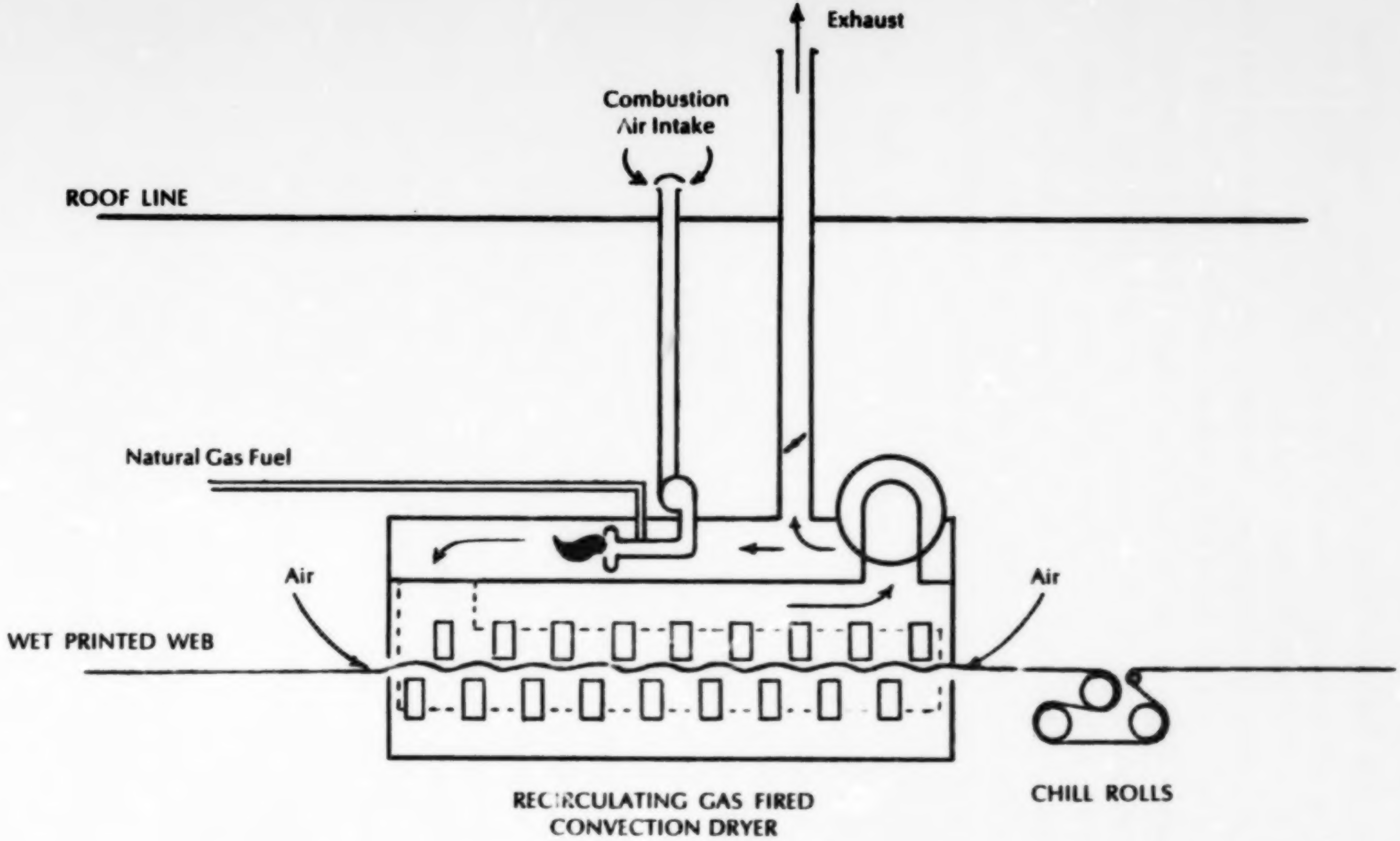
Exhaust
Combustion
Air Intake
ROOF LINE
Natural Gas Fuel
Air
Air
WET PRINTED WEB
RECIRCULATING GAS FIRED
CONVECTION DRYER
CHILL ROLLS

Figure 1. Schematic of web drying process.

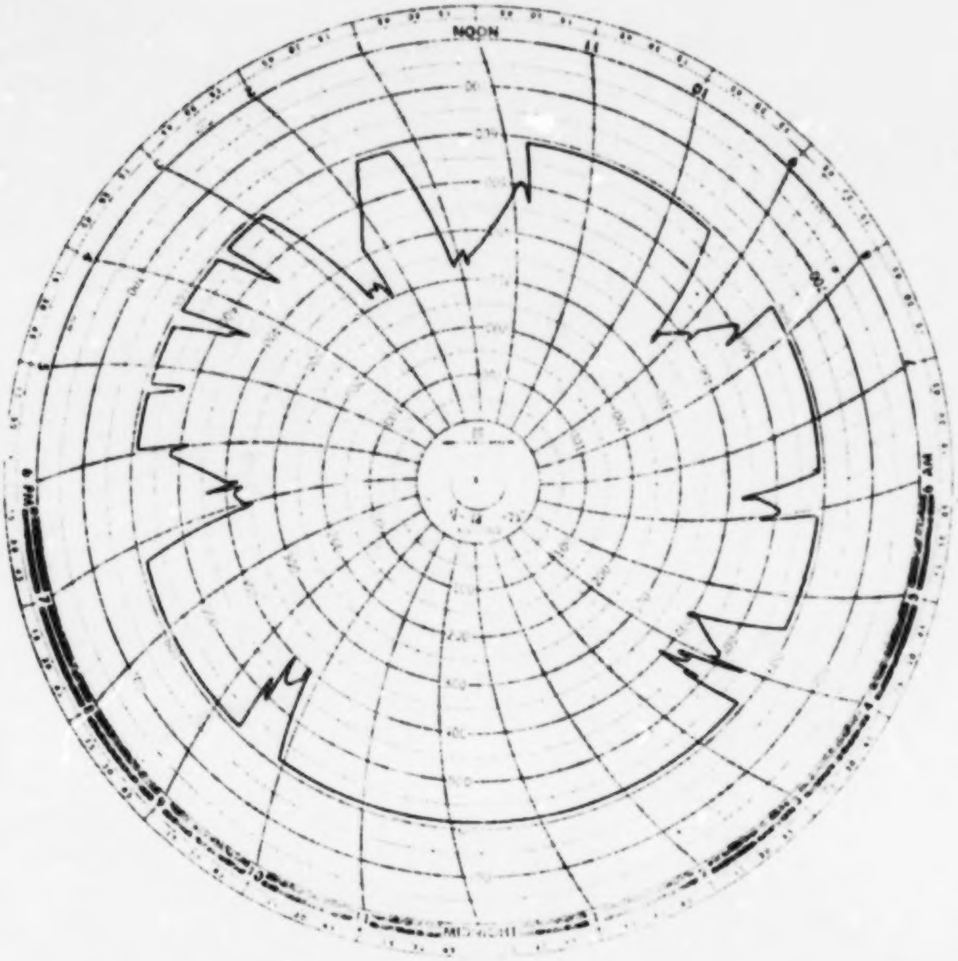

Figure 2. Typical press dryer temperature chart.

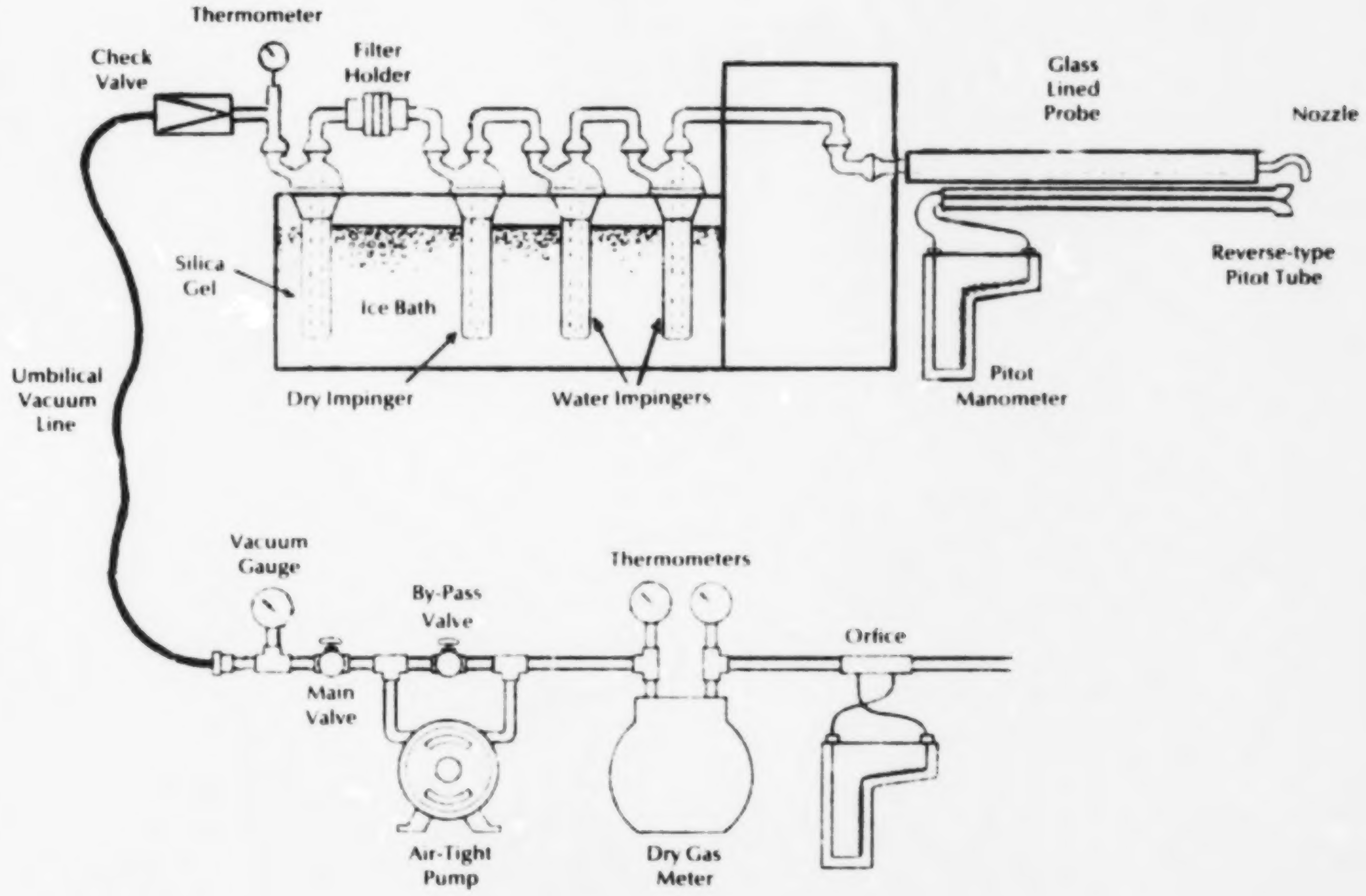
Thermometer
Check Valve
Filter Holder
Glass Lined Probe
Nozzle
Silica Gel
Ice Bath
Reverse-type Pitot Tube
Umbilical Vacuum Line
Dry Impinger
Water Impingers
Pitot Manometer
Vacuum Gauge
Thermometers
By-Pass Valve
Orfice
Main Valve
Air-Tight Pump
Dry Gas Meter

Figure 3. Schematic of modified EPA Method 5 sampling train.

purpose is to avoid interference with the physical state of the effluent mixture in which translational kinetics may have already commenced. Then too, the filter is located between the third and fourth impingers. Thus this modified approach enables the gas stream to continue cooling; this is intended to enhance aerosol formation and its subsequent impingement. Nonimpingable aerosol particles, which most generally are present, are trapped beyond the impingers where the filter has little chance of becoming clogged. The probe of course is washed to recover any contaminents that may have remained therein. The emission samples are then analyzed by conventional gravimetric techniques.

Initially this modification of EPA Method 5 was employed to survey a variety of press and dryer systems to assess the magnitude of emission problems. A typical analysis (table 1) showed hydrocarbon emissions in the range of 20 pounds per hour. Emissions from other press sources were found to be considerably lower and some were also higher. Since the initial survey, the modified impingement train has been used 42 times in the analysis of effluent gases from 15 stacks on 8 printing presses.

The question occasionally arises, why use a test method which is designed for particulates to determine hydrocarbon emissions? To date, while various instrumental methods have been promulgated (refs. 2,3), regulatory channels in general have been conspicuously silent in regard to methods for hydrocarbon sampling and analysis. In retrospect, however, the modified EPA Method 5 has certain advantages. Being isokinetic, this test is confidently applicable to effluent streams over a broad range of temperatures, including the comparatively cool exhausts from nonthermal abatement devices. Additionally, as will be shown, emission measurements correlate quantitatively with the actual collections of contaminents from control equipment. In a statistical sense, a further advantage is the comparatively large proportion of stack gases that are actually sampled in the 2-hour test period. Then too, the actual weight of contaminants is determined as opposed to the application of correction factors and comparative values in relation to reference materials.

There are of course disadvantages as well. The entrapment of

Table 1. Typical midrange level of emissions from letterpress printing

Average press operating conditions			
Printing rate		22,550 iph	
Dryer temperature		540° F	
Web temperature		295° F	
Average stack sampling conditions			
Stack temperature		414° F	
Velocity		2,150 fpm	
Flow rate		11,457 ACFM	
Effluent summary			
	Concentration (lb/SCF)	Volume rate (SCFM)	Weight rate (lb/hr)
Condensable hydrocarbons	55.82×10^{-6}	approx. 0.72	22.76
Water	11.91×10^{-4}	173.9	485.6
Dry gases	7.26×10^{-2}	6,620.5	29,597
TOTAL		6,795	30,105

contaminants is limited to materials and the concentrations thereof which are condensable at impingement temperatures. Unfortunately, the significance of noncondensables is to date unknown, since a direct comparison with other methods has not been made. A further limitation is that the time to conduct the test severely limits the amount of testing that can be accomplished in a given period of time.

MONITORING OF CONTROL SYSTEMS

This search for a systematic means of abating hydrocarbon emissions from heatset printing has been extensive. Investigations at our plant have included the compositional aspects of inks as well as a variety of control devices.

Half of the source tests made using the modified Method 5 train were concerned with efficiency studies on pilot abatement equipment. In these instances multiple tests on the input and exhaust streams of these control devices were conducted simultaneously with the use of two trains. Results of analyses with the modified train were subsequently compared with the actual collections of materials abated from the gas stream.

Various pilot systems were erected with rigid ducting to utilize a sample stream from a particular press-oven exhaust stack. After their initial startup and adjustment, these pilot systems were monitored over an extended period of continuous running. Such investigations covered from 130 to nearly 500 actual press-run hours.

Some of the more pertinent types of data which were recorded are depicted graphically in the Systems Monitoring Log (figure 4). This diagram shows several parameters of the abatement process and the press operation as well, plotted on a time base. These particular data were obtained with a pilot electrostatic precipitator system on a web offset press. The precipitators examined were of the two-stage type; that is, ionization with subsequent collection. Also, these systems were multiple effect configurations. Throughout the time period here shown, the printed form--that is, the product being produced by the press--remained the same. With the exception of dryer temperature, each data point represents the accumulated average quantity over the time period between readings or successive points. In this way the trends and relationships between various processing parameters were followed.

For example, the amount of hydrocarbon oils removed from each unit in the abatement system were measured. Here these are shown as the ratio of condensate in the heat exchanger and that of the aggregate of the oil collections from the electrostatic precipitator units. The total quantity of hydrocarbons abated from the sample exhaust stream is shown in pounds per hour of actual press operation.

Press conditions are similarily depicted in the upper three line plots, which include: the press-running time ratio, oven temperature, and the average press speed in impressions per hour.

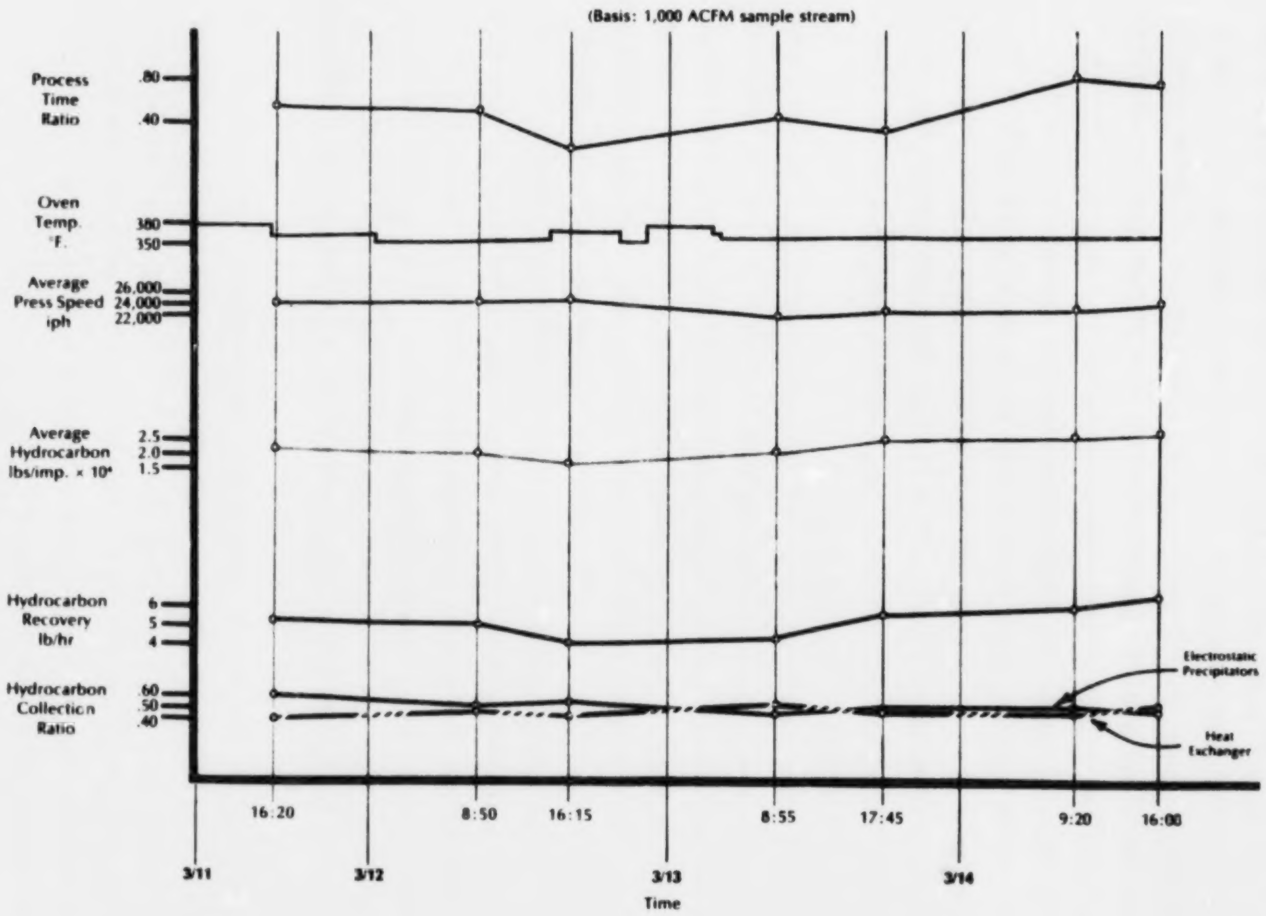

Figure 4. Systems monitoring log for web offset press and electrostatic precipitators. (Basis: 1,000 ACFM sample stream)

The centermost line in figure 4 shows the relationship of the rate of oil collection to the running rate of the press in pounds of hydrocarbons per impression. To the uninitiated it might seem that this value should be relatively constant, within some narrow range of experimental error. Not true; printing is a craft wherein numerous parameters are continually adjusted to produce a uniform product. Such adjustments are necessary to correct for the variances in raw materials as well as the drift or wear in the replacement elements (plates, blankets, packing, etc.) of the printing makeup. Thus hydrocarbon emissions deviate from the mean level, particularly over rather broad time periods.

RESULTS OF SOURCE TESTS

Monitoring operations such as these were conducted over hundreds of hours of operations with both electrostatic precipitator systems and fiber bed collectors. Data plots such as these were utilized to track their performance. With precipitator systems as well as with fiber bed collectors, equipment from more than one manufacturer was examined. Consequently, it is felt that the results can be discussed objectively in terms of the merit of contemporary technologies while the specific manufacturers remain anonymous.

Insofar as possible source tests were made in the course of a printing run so that monitoring data could be obtained before, during and after the emission determinations. For example, the two-stage electrostatic precipitator system in figure 4 was source tested in the period between 8:55 and 17:45 on 3/13. The hydrocarbon collection data for this same period were used for comparison with the emission rates determined with the modified Method 5 impingement train.

The results of source tests with four electrostatic precipitator systems are shown in table 2. The data were normalized to 1,000 ACFM input for ease of comparison. The arithmetic difference between the source tests for the input and exhaust streams is reflected in the column under Weight removed, by analyses. For comparison, the hydrocarbon removal determined from the actual material collected in the control system are labeled Weight

Table 2. Performance tests for two-stage electrostatic precipitation systems*
(Basis: 1,000 ACFM sample stream)

	Process loading		Measure of condensable hydrocarbons					Efficiencies (percent)		
			Concentrations (gr/SCF)		Weight removed (lb/hr)					
	Superficial velocity (fpm)	Percent of rated capacity	Input	Output	By analyses	Direct measure	Correlation (percent)	Heat exchanger	E.P.	Total system
System "A"	418	83.9	1.046	0.122	5.40	5.61	+ 3.9	41.4	69.2	82.0
System "B"	514	100.4	1.094	0.222	5.27	5.64	+ 7.0	33.6	65.5	77.1
System "C"	393	76.8	0.941	0.155	4.96	5.67	+14.3	32.2	74.5	82.7
System "D"	396	79.5								
Heat exchanger			1.463	0.593	2.44	2.38	- 2.2	30.5		
E.P.			0.593	0.072	4.84	4.65	- 3.9		87.3	
Comb. Total					7.28	7.03	- 3.3			91.1

*Systems A, B, and C were evaluated on web offset presses; system D was evaluated on letterpress equipment.

removed, by direct measure. The correlation between these two values is rather striking. While better in some cases than in others, the two independent data sources are in very good agreement. System "D" is particularly significant; in this instance three source tests were run simultaneously. These included the system inlet and exhaust streams as well as the gas stream between the heat exchanger and the precipitator units. These test results show excellent correlation, both for the individual processes and the overall system as well.

Although different equipment is represented, the performances of these systems are rather closely grouped. Even at less than rated capacity, however, they failed to consistently achieve 85 percent reduction in condensable hydrocarbon emissions. Moreover, while not apparent from these data, it was also conclusively demonstrated that two-stage electrostatic precipitation is quite unfeasible at the moisture level of the press exhausts from our plant.

In a further phase of these investigations, fiber bed collector systems were similarly monitored and source-tested (table 3). In these performance tests, however, comparative collection data could only be developed with two of the four systems listed. Also, a broader range of condensable contaminants was examined. As might be expected, lower concentrations diminish the possibility of hydrocarbon entrapment. At first glance the correlation between the rates of hydrocarbon collection are not quite as excellent as some of the examples covered earlier. Consider though that a fiber bed is a wetted pad; at equilibrium conditions it will drain at a constant rate. But, web printing is a random condition of running. Starts and stops are prone to produce changes, both in the rate of drainage from the pad as well as the proportion of oil and water in the drainage mixture. Under these circumstances, and with no prescribed time or condition for making the monitoring collections, correlation with the results of the source tests are reasonably good.

Even at moderate-to-heavy loadings these fiber bed systems show a considerable departure from 85-percent reduction requirements. Neither does there seem to be any improvement with reduced flow rate.

Table 3. Performance tests for fiber-bed collection systems*
(Basis: 1,000 ACFM sample stream)

	Process loading		Measure of condensable hydrocarbons					Efficiencies (percent)		
	Superficial velocity (fpm)	Percent of rated capacity	Concentrations (gr/SCF)		Weight removed (lb/hr)		Correlation (percent)	Heat exchanger	Fiber bed	Total system
			Input	Output	By analyses	Direct measure				
System "E"	8.0	88.8	0.176	0.132	0.22	--	--	Not separately identifiable		22.5
System "F"	8.1	90.6	0.372	0.123	1.35	--	--	Not separately identifiable		64.7
System "G"	31.2	102.0	0.952	0.252	3.73	4.14	+11.1	17.5	55.5	63.3
System "H"	24.6	80.0	0.820	0.231	3.21	2.95	- 7.9	18.4	56.3	64.4

*All systems evaluated on web offset presses.

In conclusion, the validity of source tests herein presented has been substantiated by independent data from actual measurements of total abatement. The value of systematic monitoring of process variables in achieving definitive results has been demonstrated. Additionally, simultaneous measurement of input and exhaust rates is a most meaningful measure of efficiency.

From a business operational standpoint these studies were expected to identify a practical method of hydrocarbon abatement; in this respect the investigation failed. These process investigations have, however, demonstrated that substantial capital investments in the technologies investigated would be futile and unjustifiable. Moreover, short of thermal abatement methods, which appear somewhat impractical for numerous reasons, an effective method of control for heatset web printing remains to be developed.

ACKNOWLEDGMENT

The efforts of Mr. George Lock of Dayton Press, Inc., in assisting in obtaining much of the data herein presented as well as in the preparation of graphic exhibits is greatfully appreciated.

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DISCUSSION

CHAIRMAN SCHAEFFER: As I promised earlier, I think it only fair at this point to entertain questions for both Mr. Fremgen and Mr. Zborovsky.

MR. RON LIPINSKI (State of Maryland, Bureau of Air Quality Control, Baltimore, Maryland): I really have two questions and a comment to make. The first is for Mr. Zborovsky. You mentioned the use of ultraviolet inks and low-temperature-drying inks as an alternative control procedure. In discussing a compliance schedule with several printing companies in Maryland, these were considered as an alternative. Both the companies indicated they were not desirable because of problems in color and sheen of the final printed product. Could you or someone else comment on whether these problems have been eliminated and whether that option is still a consideration?

MR. FREMGEN: Let me throw something in on that, if I may.

MR. ZBOROVSKY: Sure.

MR. FREMGEN: When you consider drying by the UV process, at the same time you had better consider which segment of the industry it is in. I think it was brought out in discussions, perhaps yesterday, that the industry is broadly segmented, and what may be reality in one segment of the industry can be a gross color problem in another segment.

MR. LIPINSKI: So there are individual problems then?

MR. FREMGEN: There are individual problems; I think that the ink companies can respond better to that, but there are individual problems, yes.

MR. LIPINSKI: One quick comment if I could. In the State of Maryland, where the air solvent control devices (e.g., CVM devices) were tested, regulations do call for no visible emission. And in all fairness, Joe, you mentioned that there was really no promise of the CVM device meeting air pollution regulations.

It is our opinion that the device does have potential. We evaluated the units under various conditions, as well as we could. It was not specifically tested using this technique or some other technique, but it is our opinion that with some modificiations it could be an economically viable control device, depending, of course, upon the type of regulations you have to meet. It had difficulty meeting no visible emissions, this is true. But it is our opinion that with some modifications it could even meet that.

My final question is to Mr. Fremgen. You mentioned in your evaluations of the two-stage ESP that they were not viable control devices because of the moisture content present in the exhaust stream. Could you comment on that? Were these your letterpress ovens or your web offset ovens.

MR. FREMGEN: Certainly, offset more than letterpress, but actually, both. You will actually find the performance will change with the season of the year. The season of the year determines the moisture content in the ambient air.

If you look at a press, it has several important sources of moisture. The first of these comes from the web that goes into the press oven itself. The second important source of moisture is the combustion with methane for the heating and drying. And the third source, in the case of all presses, would be the ambient air that goes into that oven simultaneously with the web. Specifically, in the case of lithography, a fourth source is the dampening solution. It tends to be a little heavier in moisture than the letterpress stream. But we found and conclusively demonstrated that with the moisture content of the exhausts at our plant, the equipment will not take it.

MR. LIPINSKI: It will not operate efficiently then.

MR. FREMGEN: It will not operate reliably. There is no point in having that dude on the roof if it will not run, it will not do the job you guys want it to do.

MR. LIPINSKI: Joe, in your evaluation of this UAS ESP, have you received similar comments that it is not a reliable control device from the other people who have utilized it?

MR. ZBOROVSKY: I have heard some information, but some people have conducted tests on the UAS system. And I think they obtained some of the results that are very much the same as what Bob has obtained in his studies. I have not seen any document evidence at this time.

CHAIRMAN SCHAEFFER: We have not done a study on that unit.

MR. FREMGEN: The real key in any of this equipment, in putting it up there and flipping a switch and looking at the plume, is that you really have to concentrate on that equipment if you want to find out how it is going to operate, what it is going to do for you. It takes intense study, and I am afraid people who act on intuition are going to spend a heck of a lot of money.

MR. LIPINSKI: Thank you.

CHAIRMAN SCHAEFFER: A question?

MR. JERRY NASS (United States Printing Company, E. Rutherford, New Jersey): This question is for Mr. Zborovsky. In your data on low-solvent, low-energy inks, your figures state as low as 25--roughly below what is normally used in conventional inks. I would like to know the speed of the press where this was taken, the nature of the job, the amount of coverage, and whether it was with substrates such as coated paper. Also, if possible, I would like to know whether it went to a sheeter or folder, and finally, if this was a field trial or commercial run?

MR. ZBOROVSKY: That is a very interesting question. I do not have that kind of information. Most of this information was supplied to me by Inmont Corporation. And I think if you are interested in this, you could possibly contact a gentleman from Inmont; his name is Joseph F. Ackerman I think he might be able to supply you with that information.

CHAIRMAN SCHAEFFER: Joe, we were involved with a test with a low-temperature, low-solvent-drying ink on a field test, not a commercial production run, which was a four-color production job. If I remember correctly, we attempted to run in the neighborhood of 800 to 1,000 fpm. But it was not a very successful run as a field test.

MR. FREMGEN: Incidentally, preprints of my paper will be available in the lobby.

MR. BRUCE LAMM (Fawcett Printing Corporation, Rockville, Maryland): This is directed to Mr. Fremgen. You stated that the system will not handle moisture. Yet in the two-stage electrostatic precipitator, you are actually adding moisture to reduce the temperature, because the unit will not accept temperatures higher than 200°.

MR. FREMGEN: I am not using moisture as a cooling device. I am using indirect cooling. I did not add moisture to the stream. This particular system, as a substitute, was cooled with a water tube heat exchanger. This was only a substitute because pilot air-to-air heat exchangers are rather difficult to come by.

MR. LAMM: We are in the process of adding the electrostatic precipitator to two of our presses. And we are getting what we call the sonic heat exchanger, which is nothing but a controlled water spray.

MR. FREMGEN: Right.

CHAIRMAN SCHAEFFER: Any other questions?

GENERAL CHAIRMAN FISHER: Mr. Zborovsky, you mentioned among the systems an activated charcoal system. One of the things that bothers me about these activated charcoal systems is their need for regeneration. If you use a hot air regeneration technique, really all you do is collect the material and let it out; you are not running other operations.

Do you have any information on exactly what process they are using to regenerate the charcoal, and what controls they are placing on the effluent from the regeneration?

MR. ZBOROVSKY: The activated charcoal system that Los Angeles Lithograph Company is utilizing is a patented process where they have electrical heating elements in each bed. They are using a vacuum system on this, where they pull the vacuum down to about two torrs, or about two millimeters of mercury. By lowering the pressure or pulling the vacuum down on each bed and increasing the temperature of the bed, they are able to flash-off these hydrocarbons. They have a condensation system which is a series of condensers--first watercooled condensers and then a refrigeration system--which brings the temperature down to maybe -40° F.

The hydrocarbons that are recovered then in the collection tanks are trapped. And just by the different temperatures of these condensers, they are able to get an effective separation between the high boilers and the low boilers rolls that are entrapped on the activated charcoal.

I do not think that there are any problems that I can recall in regenerating these particular systems other than some of the operational problems they have in the actual design of the equipment. They are plagued with a series of leaks, temperature drops, and temperature control. That is the major problem with this particular type of system. Other than that, it seems to be a very reliable system, providing these problems can be eliminated.

MR. FREMGEN: Consider also the fact that the vacuum installation is unique. It is not like the systems used for gravure operations at all. The carbon bed can get clogged up with a lot of resinous material. Replacement of carbon is neither inexpensive nor easy.

MR. ZBOROVSKY: If there has not been adequate temperature control in that particular bed, there will be some condensation of some of the resinous material. You get some plugging or channeling in the bed.

CHAIRMAN SCHAEFFER: I think we have had two very interesting sessions in looking at the Environmental Impact of Chemicals Used in the Printing Industries. I want to thank the speakers for their very effective presentations and you, the audience, for your active participation in the program.

23 September 1975

Session III:

IMPACT OF WASTE RECOVERY AND RECYCLING ON THE ENVIRONMENT

Robert L. King[*]
Chairman

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[*] General Engineer, Office of Enforcement, National Field Investigations Center, Environmental Protection Agency, Denver, Colorado

SESSION INTRODUCTION

Robert L. King
Session Chairman

In this session, the first two speakers talk in terms of two areas. One is monitoring of wastewater effluents; the second looks at the new dirty word in EPA, PCB's. The meaning is fairly well hidden, but behind the title are sources of toxic chemicals.

MONITORING OF LIQUID EFFLUENTS FROM THE GOVERNMENT PRINTING PLANT

A. R. Materazzi, Ph.D., and J. U. Gouin*

Abstract

The program of monitoring our effluent water has given us a firm picture of the quality of our effluent, as well as an opportunity to work with test procedures stipulated by the Environmental Protection Agency. We found that in our laboratories two of these procedures had to be modified slightly in order to avoid ambiguous results. Nearly all of our effluents were within ranges acceptable to Government standards. The monitoring program continues but at a reduced rate. We think that we can improve the one or two problem areas indicated by our tests and that we should be able to comply with the proposed EPA regulations. Despite our heavy consumption of water, which will tend to dilute any contaminants entering the effluent, we feel that the results we have obtained are indicative of what can be expected by the printing industry in general.

The United States Government Printing Office was established in 1861 in order to provide printing services required by the Congress. The first Government Printing Office was housed in a four-story wooden structure containing 60,000 square feet of floor space; it housed 26 printing presses and 4 pieces of bindery equipment. Three hundred and fifty employees produced Congressional printing valued at approximately $500,000.

Today the Government Printing Office occupies three eight-story buildings and one four-story building, which have a combined floor space of more than 32 acres. It employs 8,500 people and produces or procures printing and binding for the Federal Government valued at nearly $500 million in fiscal year 1975. Even though almost 70 percent of the printed products are procured from commercial printing sources, the remaining 30 percent is considerable. To accomplish the in-house work, it utilizes 340 composing and casting machines, 2 high-speed photocomposing systems known as the

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*Albert R. Materazzi, Manager, Quality Control and Technical Department; and J. U. Gouin; U.S. Government Printing Office, Washington, D.C.

Linotron 1010's, 240 pieces of bindery equipment ranging from wire stitching to automated binding lines; 42 offset presses, and 83 letterpresses. The most modern piece of equipment is the optical character reader and test editing system, which greatly augments the output of the Linotrons.

Several types of relief plates are made, including photopolymer and stereos in addition to copper, zinc, and magnesium engravings. Over 85,000 aluminum offset plates are used in 1 year and 1 million square feet of photographic film. The paper required to produce this work requires nearly 7 freight cars and more than 11 truckloads each day. We manufacture 200,000 pounds of ink in a normal year and buy another 300,000 pounds. We make most of our own adhesives and have our own carpenter, electrical, sheet metal, and machine shops.

With the exception of flexography and gravure, the Government Printing Office can be considered a microcosm of the entire printing industry of the United States. Thus it can be argued that our experiences with problems associated with the environment reflect those of the industry. The results we obtained in monitoring our water effluents should be of interest and, if typical, they would indicate that the printing industry is not a significant contributor to the pollution of our water resources. The threefold purpose of this paper is to document our experiences describing the test methods utilized, to list the results obtained, and to compare them with proposed EPA effluent limitation guidelines for discharge to surface water of process waste pollutants of the paint, ink formulation, and printing industry.

During the fiscal years 1972 through 1974 the water consumption of the Government Printing Office averaged 240 million gallons per year. Eventually all of this finds its way into the District of Columbia sewage treatment plants. It is not possible to break out the specific amount of water used by the manufacturing processes at the Government Printing Office. In a general sense we know that a considerable portion of the water is used for cooling purposes in linotype and monotype composing machines, in the making of stereotype plates, and in the chill rollers of web offset presses. A great deal of water is used in the production of negatives and offset plates. Also, significant users are in photoengraving, electrotyping, the type metal foundry, and the inkmaking section. When we consider the needs of over 8,000 employees and the industrial cleaning required for 32 acres of floor space, it is no wonder that on an average 24-hour working day approximately 33,000 gallons of water per hour are used by the Government Printing Office.

There are no regulatory limits on the quality of water being discharged by large industrial users in the District of Columbia. Section 307B of the Water Pollution Control Act of 1972 (Public Law 92-500) requires the Federal Government to establish regulations concerning the discharge of process wastewater by industry. EPA has published proposed effluent limitation guidelines for the paint, ink formulation, and printing industries which are presently being reviewed and are targeted for adoption some time in 1976. The District of Columbia is waiting for limitations to be published regarding discharge into sewage systems before issuing its own regulations. It may adopt Federal regulations or modify them as the local situation requires.

Consequently the Government Printing Office began to analyze its effluent water early in 1975 in order to establish what problems might be encountered in meeting the proposed standards. In addition, the information was required for the environmental impact study currently in preparation looking forward to a new Government Printing Office early in the 1980's. What follows is a report of the procedures and methods used and the results we have obtained thus far, followed by a discussion of what we have learned from this preliminary work.

Six discharge points in the Government Printing Office complex were selected based on ease of availability and because they were the identical points used for a special sampling conducted by the District of Columbia Government during the summer of 1974. These points are shown in figure 1 and are assigned Roman numerals I through VI on table 5. Two men were used to procure samples, which were taken by dangling a collapsible 1-quart plastic container at the end of the strong twine into the effluent water. Some 1-1/2 to 2 hours were required to procure samples at all six locations.

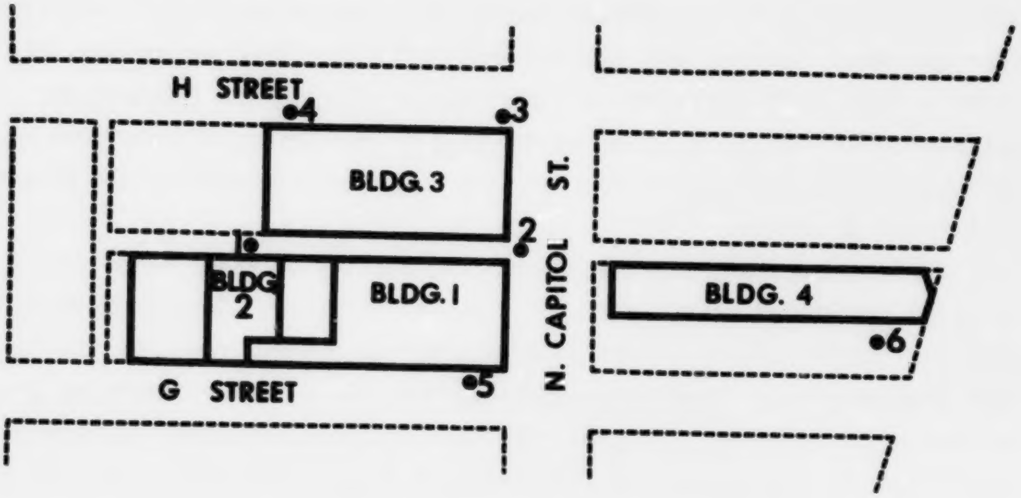

Figure 1. Combined sewer effluent sampling location, U.S.G.P.O., Washington, D.C.

The containers were delivered to the laboratory and analysis usually began the same day. Initially we used methods and procedures taken from Standard Methods for the Examination of Water and Wastewater," 13th edition, (ref. 1), and "Methods for Chemical Analysis of Water and Wastes," 1971, published by EPA (ref. 2). Some changes in these procedures became necessary; these will be pointed out later on. The results were compared against the proposed EPA limitations. The intent was that if we had found significant variations from these standards, corrective action would be taken. None was necessary.

Table 1 shows the metal concentrations obtained in these tests. Initially the analyses were made using an atomic absorption spectrophotometer, model 403, built by the Perkin-Elmer Corporation. Suspended solids were removed prior to analysis. All of the samples to the left of the bold line are those that we determined to be below the concentration of the proposed limitations and those to the right are over the limitations. It should be pointed out that all of the lead determinations of the 60 samples whose concentrations are listed in the 0.05 to 0.10 mg/l category were placed in that column because the detection limit of the spectrophotometer

Table 1. Heavy metals analysis

Element	Proposed limitations[1]	Conc. in tap water[2]	<.05 mg/l	.05-.10 mg/l	.11-.5 mg/l	.51-1-0 mg/l	1.1-5.0 mg/l	>5.0 mg/l
Lead	.05	<.1		60	5		1	
Chrome	.5	<.05	43	7	3	2	2	2
Copper	.5	<.05	33	13	15	1	1	
Zinc	.5	<.05	43	6	11	2		
Iron	1.0	<.10		32	17	4	1	
Manganese	1.0	<.05	53	3	6			
Magnesium	100.0	5.5					13	47

[1] Proposed EPA effluent limitations for discharge of process wastewater pollutants expressed in milligrams per liter.

[2] Numbers in columns refer to number of samples analyzed which had that concentration.

Table 2. Lead determination by A. A. using furnace (flameless method)

Date	Proposed limitation*	I	II	III	IV	V	VI	Tap water
8/25/75	.05	.008	.004	.003	.006	.003	.002	<.001
8/26/75		.019	.009	.002	.008	.004	.014	<.001
8/28/75		.022	.005	.001	.016	.002	.004	<.001

*Proposed EPA effluent limitations for discharge of process wastewater pollutant.

NOTE.-Numbers in columns are mg/liter.

using the air-acetylene flame was only 0.10 mg/l. Subsequently we obtained a furnace which extends the lower limit capability well below the 0.05 mg/l limit. Table 2 shows the results obtained using this instrument modification and shows that we are well below the proposed standard. Since the Government Printing Office manufactures or recycles over 12 million pounds of type metal that is approximately 83 percent lead, we were pleasantly surprised.

The next item of concern was the chromium content; 10 percent of the samples were over the recommended standard. Very little chromium enters the effluent from the manufacturing process, a very minor amount from offset press fountain solutions, and a smaller quantity from the rinsing operations in electroplating. We now feel that the chromium found comes from rust inhibitors incorporated in the water in our air-conditioning towers. The air-conditioning system is being replaced and this situation should correct itself.

The only other element we expected to be a problem was zinc coming into the system from offset press fountain solutions, the diazo salts used in offset plate sensitizers and zinc etchings. Only 2 out of 62 samples were above the proposed minimums. Surprisingly, considering the occasional hard water encountered in the District of Columbia and the number of magnesium plates made, all of the samples were below minimum in magnesium content.

Results for organic substances, suspended solids, and pH are shown in table 3. Seven different samples were taken at seven different times at each of the six sampling points. Once the determinations were made the results were averaged. However, only three samples taken at three different times were used for the oils and greases because of a problem with the test method.

Even though the proposed standards have no limits for chemical oxygen demand (COD), we made these determinations and they are listed in table 3. It is not possible to assign to the manufacturing process an established percentage of this value since the water from the manufacturing process and that used for the elimination of human waste are discharged together into the effluent.

It is readily apparent that we have no problem with pH despite the use of caustic cleaning agents in our ink section and the use of acids in photographic and etching operations.

Nor is any problem indicated with phenols. We did fail to comply with the proposed standards for suspended solids in five of the six sampling points. We are currently trying to determine the source of these solids. One possibility is the lacquer developer used in offset platemaking, which

Table 3. Miscellaneous water analyses

Analysis	Proposed limitations[3]	I	II	III	IV	V	VI	Hi	Lo
pH	6-9	6.94	7.43	7.56	6.40	7.44	7.58	8.1	3.7
Suspended solids[1]	30	26.0	121	70.0	229	51.0	76.0	494	.1
Phenols[2]	100	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	2.5	-
Oils & greases[1]	10	23.6	67.0	19.7	142.9	25.5	53.0	3.2	252.8
Chemical oxygen demand	None given	124	301	48	512	317	240	875	24

[1] Numbers are milligrams per liter.

[2] Numbers are micrograms per liter.

[3] Proposed EPA effluent limitations for discharge of process wastewater pollutants.

Table 4. Suspended solids (all samples are from Sample Point IV only)

Date	Proposed limitations[3]	10:00[1]	10:10	10:20	11:00	11:10	11:20	Average
8/18/75	30	63[2]	199	28	102	63	246	117
8/20/75		45	214	104	-	456	258	215

[1] Column headings are the actual times samples were taken in the A.M.

[2] Numbers are milligrams per liter.

[3] Heading is proposed EPA effluent limitation.

contains considerable quantities of insolubles. However, we had a large variation in results, so on two occasions we sampled at 10-minute intervals. Table 4 shows the results with still a large variation. We suspect that the variations are probably not due to the manufacturing process but to an inadequacy of the sampling method which could include large undispersed agglomerates. In any case, the sampling techniques employed are going to have to insure that the sample is dispersed and representative of the manufacturing waste only. If the waste can agglomerate, it would not be representative. In that instance, sampling at consecutive brief intervals may give more meaningful results. We intend to pursue this line of investigation further.

Oils and greases were above proposed limitations but since cafeteria waste and human waste are included, no firm conclusion can be reached.

Table 5 lists the results of lead determinations compared with lead content in tapwater and is included to show the degree of sophistication required for analysis. Only the six circled points exceeded the amount contained in tapwater. These determinations were made with the acetylene flame before we acquired our furnace for the atomic absorption spectrophotometer and we have not had time to repeat the work with the electric furnace. However, this pinpoints a problem in sampling, since it is obvious

Table 5. Lead analysis

Date	I	II	III	IV	V	VI	Tap
2/11/75	<.1	<.1	<.1	<.1	<.1	.4	<.1
2/20/75	.29	<.1	<.1	.34	.13	.15	<.1
2/28/75	<.1	<.1	<.1	<.1	<.1	<.1	<.1
3/8/75	<.1	<.1	<.1	<.1	<.1	<.1	<.1
3/12/75	<.1	<.1	<.1	<.1	<.1	<.1	<.1
3/18/75	<.1	2.64	<.1	<.1	<.1	<.1	<.1
3/21/75	<.1	<.1	<.1	<.1	<.1	<.1	<.1
6/6/75	<.1	<.1	<.1	<.1	<.1	<.1	<.1
6/17/75	<.1	<.1	<.1	<.1	<.1	<.1	<.1
6/27/75	<.1	<.1	<.1	<.1	<.1	<.1	<.1
7/16/75	<.1	<.1	<.1	<.1	<.1	<.1	<.1

NOTE.-Numbers in the columns are milligrams per liter.

had we not sampled the week of February 20, 1975, we would have been in compliance at all but two points. From this, one should conclude that some consideration will have to be given to the time lapse between samplings. As was pointed out earlier, once we increased the sensitivity of our instrument we were well below the proposed limits.

Discussion of test methods

Two of the test methods recommended by the literature gave us a problem. The first was the colorimetric method utilized for the determination of phenol. This method is based on the use of 4-aminoantipyrine, which reacts with phenol to produce a characteristic color that can be extracted with chloroform. The absorption of the extraction at a selected wavelength is measured in a colorimeter. The instructions in the literature indicate that the 4-aminoantipyrine is added first, followed immediately with the addition of potassium ferricyanide to avoid the color coupler being oxidized by agents present in solution. When this happens, the color reagent becomes darker in color and even unreacted dark color reagent would be extracted, resulting in high readings. Both the reacted material and the original color coupler are extracted by chloroform. We found higher values when running blanks with distilled water and tapwater than those of the samples being analyzed. By reversing the addition of the reagents, i.e., by adding the potassium ferricyanide first, the results obtained with the distilled water and tapwater blanks were sensibly lower than the samples. We now use this procedure in analyzing for phenol.

We theorize that dissolved oxygen in water was causing our problem and it was prevented from reacting with the color reagent by adding the antioxidant first. We plan at some future time to prove this hypothesis by using distilled water saturated with an inert gas--for example, argon.

The EPA "Methods for Chemical Analysis of Water and Wastes" specifies the procedure for analyzing for oils and greases and requires that the acidified sewer sample be filtered through muslin cloth and diatomaceous earth. The filter pad is transferred to an extraction thimble and placed in a Soxhlet extraction apparatus and extracted by refluxing for 4 hours with hexane. The solvent is driven off the extracted material and the amount of oils and greases determined gravimetrically.

A problem was encountered using this method. Extraction performed using distilled water and tapwater in place of the sewer sample also gave high results. The I.R. curves of the water extractions were compared with a hexane extraction of the muslin and filter aid; they were identical. We were forced to assume that they contained hexane soluble materials.

We then tried an alternate procedure from "Standard Methods for "Examination of Water and Wastewater." This involved extracting the acidified sample with hexane in a separatory funnel. The supernatant liquid was filtered through No. 40 filter paper into a beaker, evaporated, and the amount of oil and greases was then determined gravimetrically.

When this method is used with tap or distilled water, a negligible amount of residual material remains in the beaker. More important, the I.R. curves of sewer sample extractions are different than those obtained with the muslin-filter aid extraction method. We consider this method to be much more reliable.

Summary

The program of monitoring our effluent water has given us a firm picture of the quality of our effluent, which we could only estimate previously. It also gave us an opportunity to work with the test procedures stipulated by the Environmental Protection Agency. We found that in our laboratories two of these procedures had to be modified slightly in order to avoid ambiguous results. The monitoring program continues but at a reduced rate. We think that we can improve the one or two problem areas indicated by our tests and that we should be able to comply with the proposed EPA regulations. We also feel that despite our heavy consumption of water, which will tend to dilute any contaminants entering the effluent, the results we have obtained are indicative of what can be expected by the printing industry in general.

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COMMENT GIVEN AFTER PRESENTATION OF THE PAPER

Albert R. Materazzi

After listening to the papers presented thus far, I would like to make a few observations and present for your consideration a few caveats in light of Dr. Fisher's comments yesterday.

A casual count of the speakers during this conference breaks down to 9 from the governmental sector and 24 from the industry or its suppliers. I include Bob Praskievicz and myself in the industry sector for obvious reasons.

Industry speakers have uniformly presented what I consider to be well-researched and documented papers, with little or no attempt to disguise the warts. They have shown a keen awareness of the need to protect the environment, their employees, and their customers--the consumer. They have done their homework well and demonstrated excellent knowledge of existing, proposed, and rapidly changing guidelines. The speakers from the governmental sector have not (and I admit to some lack of objectivity) shown a similar knowledge of the printing industry or a sensitivity to its problems. Admittedly it is not as easy to understand the "fragmented" printing industry as it is to understand a well-written proposed standard in the Federal Register; but we have heard a 25- to 30-year-old monograph on inks cited as an authority; we have heard our unions cited as authority for the number of employees in the industry; and overall it seems that the industry was researched in the Encyclopedia Brittannica. If I exaggerate, I apologize.

While I realize that since Macy does not tell Gimbels, one should not expect to get good information on Macy from Gimbels, I still submit that the sometimes conflicting Environmental Protection/Employee and Consumer

Safety regulatory bodies and the printing industry should not have the same competitive relationship that Macy and Gimbels have--nor should it be an adversary relationship.

You have heard the industry characterized as a $22 billion industry and I assure you that the figure is on the low side. According to the Federal Reserve Board index of Industrial Production, the industry accounted for close to 8 percent of the total industrial production in the 1967 index year and it was growing at a faster rate than the index. In August of 1975, the index for all industrial production stood at 112.9, while that for SIC Code 26 and 27, the Paper and Printing Industry, stood at 108.9.

The industry is in trouble and is still in an economic slump. Several speakers have pointed out the fragmented nature of the industry, and the number of "mom and pop shops." Their dependence on suppliers and trade associations is almost complete in the area of ecology, employee protection, and consumerism. As has been demonstrated, the industry research groups are doing an excellent job and an inordinate amount of their time is consumed in these problems. And I am sure I speak for all of them. Do not hesitate to go to them for real information or to check data. I think I speak for the Public Printer and GPO when I say we will be pleased to cooperate in any reasonable, well-defined experiments designed to improve our environment.

If you will permit a personal note, I came into lithography 35 years ago. At the time we were extensively using wet plate photography, which used a collodion binder on glass (gun cotton in ether and alcohol) sensitized with silver nitrate. After exposure, it was developed with ferrous sulfate and fixed with sodium cyanide. It was intensified by bleaching in a mercury or lead salt and redarkened with a solution of sodium sulfide. Pressmen were routinely using carbon disulfide to regenerate rubber blankets and rollers; strippers were routinely using carbon tetrachloride to clean film. All of these were gone long before the regulatory bodies came into existence in 1970. The point is that the graphic arts industry was working to improve itself long before EPA, and was doing a pretty good job.

It was Montaigne who pointed out, "There were never in the world two opinions alike, no more than two hairs or two grains; the most universal quality is diversity." And with that I heartily agree, but let me quote to you from an address by the late President John F. Kennedy: "Let us not be blind to our differences--but let us also divert attention to our common interests and the means by which those differences can be resolved. And if we cannot end our differences, at least we can help make the world safe for diversity."

I trust that everyone attending this conference was listening and that he does not leave here without a broader view of the problems which face us in protecting this narrow, fragile biosphere in which we live without crippling an important industry whose products are still the most important means of communication ever devised by man.

DISCUSSION

GENERAL CHAIRMAN FISHER: As General Chairman of this conference, I suppose I really cannot let a malignment of the program go without comment. Dr. Materazzi is, of course, entitled to his opinion, but I must say I find it very discouraging that he seems to take the attitude that "If you do not know as much about printing as I do, you have nothing to tell me."

It is true that some of the speakers on this program are not experts in the printing industry, but they are all here because they are experts in something. And they have information which we feel should be of interest and importance to you. People like Dr. Kay and Dr. Herbert are not printers. Nobody ever said they were, nobody pretended that they are. They are experts in their own field of investigation. And they have been working in areas which happen to impact on the printing operation. We feel it is perfectly proper and that you should be aware of what they have found. They have found things which, with all your expertise in the printing industry, you probably never would have found because you are not an expert in epidemiology, toxicology, and so on.

I find it a little surprising that I hear the attitude, "These people are not qualified to talk to me." I realize that not all of us think that all of the papers are of equal quality, but I think that on the whole the papers have been good; I think they have been pertinent and I think all the speakers have contributed to our knowledge.

DR. MATERAZZI: I have no further comments beyond to say that I did not intend to be critical of the papers that you mentioned. But I was critical of the application to the printing industry based on what appears to me to be insufficient knowledge of the industry as such.

I think that they could have gotten far better inputs had they gone to Dr. Schaeffer, to Harvey George, to Paul Borth, to any number of people that are here from the industry, or to our suppliers.

Al Jasser back there has been looking out after the environment and the safety of the industry long before OSHA was dreamed of. Jackie Fetsko's work, I think, speaks for itself. This is the type of thing that I am talking about. And while I have no objection to people telling me what the carcinogens are in the industry, I submit we knew they were there. Somebody had to tell us, and they are still trying to tell us what the limits are.

DISCUSSION OF POLYCHLORINATED BIPHENYLS IN WASTE STREAMS FROM PAPER RECYCLING

Karl E. Bremer*

Abstract

Current data on polychlorinated biphenyls (PCB's), a family of chlorine-containing organic chemicals, indicate that effluents of waste paper recycling mills contain variable concentrations of PCB's. Surveillance of the industry demonstrated that 7 of 14 waste papers destined for recycling contained .1 to 3.6 ppm PCB. These waste papers represented 50 percent of the waste papers recycled at a particular mill. Current documentation suggests that mill waste treatment systems, which effectively remove particulate matter, may remove PCB's.

INTRODUCTION

Polychlorinated biphenyls (PCB's) were first manufactured commercially in 1929. In the United States, PCB's have been manufactured by a single producer, the Monsanto Industrial Chemicals Company. In addition, PCB's are manufactured in Great Britain, France, Germany, the U.S.S.R., Japan, Spain, Italy, and Czechoslovakia (ref. 1).

PCB's have been used in the following broad types of applications during the past 40 years (ref. 2):

1. "Open-ended" applications; for example, in paints, specialty inks, paper coatings, plastics, etc.
2. "Nominally closed" applications; for example, as the working fluid in hydraulic or heat transfer systems.
3. "Closed electrical system" applications, specifically as the insulating fluid in certain kinds of transformers and capacitors.

The Monsanto Industrial Chemicals Company has marketed chlorinated biphenyls under the trademarks Aroclor 1221, 1232, 1242, 1248, 1254, 1260,

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*Chairman, Lake Michigan Cooling Water Studies Panel, U.S. Environmental Protection Agency, Chicago, Illinois.

1262, and 1268. The latter two digits designate the percent chlorine of each formulation (ref. 3). During the period 1963-1971, U.S. domestic sales of Aroclor 1242 and 1254 were higher than other Aroclors. Aroclor 1016 is currently replacing Aroclor 1242 as a capacitor impregnant (ref. 2).

Current data for 1974-1975 indicate that PCB residuals have been found in fish from the marine coastal areas of the East and West, from the riverine environment, including the Mississippi, Ohio, and Hudson Rivers, and from the Great Lakes Basin, including Lake Superior, Lake Michigan, and Lake Ontario.

Current data for 1974-1975 further indicate that PCB concentrations in Lake Michigan coho salmon, lake trout, and chubs exceed the Food and Drug Administration's temporary tolerance level of 5 ppm. These concentrations have not decreased since 1972, although Monsanto has indicated limiting sale of PCB's to manufacturers of sealed electrical equipment such as transformers and capacitors. Past and more recent data demonstrate that loss of PCB's to the environment constitutes an environmental and human health hazard and is a direct cause of economic loss to the commercial fishery.

HEALTH EFFECTS

In 1968, a reported 1,000 Japanese were adversely affected after consuming rice oil containing an estimated 2,000 ppm of PCB's. During food processing of the rice oil, leaking hydrolic fluid had contaminated the oil. Japanese consuming the oil exhibited symptoms including eye discharges, acne-form lesions, and skin pigmentation problems. Pregnant women suffered miscarriages, and in childbirths, transplacental transfer of PCB's to infants was observed.

Recently, the effects of PCB's have been demonstrated in subhuman primates (rhesus monkeys) (ref. 4). In studies at the University of Wisconsin Medical School, six adult female rhesus monkeys were fed Aroclor 1248 at the level of 25 ppm for 2 months. Facial edema, alopecia, and acne were developed within 1 month, and one animal died as a result of PCB intoxication 2 months after removal from the experimental diet. These observations and others during the 1974 study attest to the toxicity of short-term, low-level exposure to PCB's in subhuman primates. More recent data have been obtained at the 2.5- and 5-ppm level (ref. 5). General observations of subhuman primates subjected to prolonged consumption of Aroclor 1248 at these levels were the following: alopecia, acne lesions, loss of weight, increased secretion of total urninary ketosteriods, irregularities in menstrual cycles, impaired ability to maintain pregnancy, and undersized infants.

Detailed presentations of biological effects on man (metabolism, toxicology, and results of human exposures) and biological effects on animals other than man have been developed by the Interdepartmental Task Force on PCB's (ref. 1). It is of interest that these and other studies demonstrate that rats tolerate PCB consumption at the 100-ppm level; subhuman primate studies show that the 100-ppm level is lethal and that the effect level is 2.5 to 5 ppm.

PCB'S IN WATER AND BIOLOGICAL ACCUMULATION

As indicated by data on residual PCB's in fish, water is a principal sink and transport mechanism for PCB's. Studies during 1971-1975 indicate that, in industrialized areas, wastewater-treatment-plant effluents are major point sources of PCB discharge to surface waters. Because biological accumulation of PCB's by fish and other aquatic organisms has been documented as greater than 40,000 and 75,000 times the exposure level, respectively (ref. 6), it is recommended that PCB's do not enter the receiving waters at detectable concentrations. (Currently detection limits range from .02 to .05 ppb.)

During the Spring of 1975, the Wisconsin Department of Natural Resources analyzed, as a part of their ongoing surveillance program, a number of discharges to Green Bay and Lake Michigan (ref. 7). Concentrations during this survey ranged from <.1 to 18.5 ppb. Because PCB concentrations were high in effluents of paper recycling mills, inplant investigations were requested of the industries. Analysis of 14 wastepaper samples indicated that 7 wastepaper grades contained PCB's ranging from .1 ppm Aroclor 1254 and .5 ppm Aroclor 1242 in heavy printed bleached Kraft to .4 ppm Aroclor 1254 and 3.6 ppm Aroclor 1242 in sorted office wastepaper. The seven wastepapers containing PCB's represented 50 percent of the wastepapers recycled at a particular mill. In addition, it was speculated that the majority of these wastepapers represented office waste forms, NCR carbonless paper, and ledgers from old files, which would date back to the period when PCB's were used in the manufacture of carbonless papers.

The Wisconsin Department of Natural Resources, in a continuing monitoring program, tested the effluents of 16 pulp and paper mills. Analysis demonstrated that nine mills had discharges of PCB's ranging from .1 to more than 18 ppb. The higher concentrations of PCB's were found in effluents of two mills which deink and recycle wastepapers.

The Central Regional Laboratory of the U.S. Environmental Protection Agency in Chicago has, and is currently assisting Wisconsin and other States in the Great Lakes Basin. The laboratory is currently involved in analyses of common forms and inks, and in analysis of PCB's in air.

CONTROL

As a suggested means of reducing PCB concentrations in waste streams I would like to present an excerpt from the recent Wisconsin Hearings on PCB's. This short presentation (ref. 8) was developed by Francis Early, a physical scientist of the Environmental Protection Agency.

Mr. Early states: "A problem of real concern at this time must be the relatively high discharge concentrations from certain Pulp and Paper mills which deink paper.

"For the record, let me briefly sketch in words the general processes used for deinking paper. The deinking pulp producer buys waste paper, which is carefully selected for the end product paper which he intends to make from the deinked pulp. These waste papers are slurried in hot water with wetting agents or dispersants and an alkaline or acidic agent to adjust the pH. Other chemicals are used as required. Once slurried, the paper, now undeinked pulp, is screened and cleaned to remove undispersed material, pieces of metal, and grit. The actual deinking takes place in a series of washers which are usually operated with countercurrent process streams. The undeinked pulp enters the system of washers at one end while clean water is introduced at the opposite end. The deinked pulp and dirty water are discharged at opposite ends. A primary objective of this process is to recover a quality fiber free from all inks, chemicals and pigments. As required by the needs of the end product paper, one or more stages of bleaching may be used.

"Where do PCB's enter this process? In the waste paper which is the raw material for the process. They are discharged with the dirty water because they are essentially associated with and attached to the pigments and inks removed during the deinking process.

"Having removed the undesired material with water the processor now has to remove them from the water before discharge to the public waters or recycling to the process.

"These waters can be given primary and secondary treatment in order to meet the requirements of N.P.D.E.S. permits, which require close control of Biologic Oxygen Demand and Suspended Solids, along with other requirements.

"There is extensive literature on the presence of PCB's in water and their introduction into the food chain. However, few of these address how it is present. However, Dr. W. Peter Schoor of Gulf Breeze Environmental Research Laboratory, in an article to be published in 1975, in England in the scholarly international journal Water Research, has demonstrated that Aroclor 1254 is soluble in water at a concentration of less than 0.1 part per billion. What this means is that any amount of this material present in water greater than this miniscule amount must be either in the suspended solids portion or in the form of an emulsion stabilized by a surface active agent. Since only a very small portion of the total amount of PCB material can be in the true solution state, limiting the discharge of these materials in paper deinking plants can be greatly enhanced by improved suspended solids removal and effective secondary treatment for removal of the oxygen consumptive material.

"The effect of improved suspended material removal on PCB discharge is intuitively evident, since a significant portion of the PCB is undoubtedly attached to the suspended particles because all PCB's are extremely lyophobic in water, and therefore have a strong tendency to coalesce with other lyophobic materials and to adhere to lyophic sites on suspended particles.

In conclusion, I think we can say that, although PCB discharges from these deinking paper mills now tend to be rather high, we can look forward to significant reduction in discharge concentrations as the programmed and projected treatment systems required by the N.P.D.E.S. program become effectively operational.

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DISCUSSION

MR. WILLIAM S. BEGGS (New Jersey Department of Environmental Protection, Trenton, New Jersey): I have several questions. Number one, can you give some idea what kind of test methods are used to detect these PCB's?

MR. BREMER: Generally mass spectrophotometry and gas chromotography are used. There have been some updates on the methods, (and maybe I am going a little bit to far here) but there is an open debate right now on detection levels. The detection levels that I presented in this report are those detection levels from the Duluth National Water Quality Laboratory and from the Central Regional Laboratory of the EPA.

MR. BEGGS: Was there some sort of concentration requirement necessary before you went to Mass Spec (sic), perhaps a GC discharge to the Mass Spec or something like that? In other words, there is a technique I know that has used capillary GC equipment to go right into the ionizing region of the mass spectrometer. Well, you tell me.

MR. BREMER: Actually, to be honest with you, I do not perform the analysis. I know that the scanning is done by Mass Spec. Samples are extracted and subjected to gas chromotography. I do not actually perform these analyses. Possibly I could take your question back to one of the laboratory people.

MR. BEGGS: I have one other question. I think you indicated that PCB's were associated with the pigments. That is how they got into the chain in the first place; is that correct?

MR. BREMER: Historically, we know there were high concentrations of PCB's in the NCR carbonless carbon paper forms. And if you take the carbonless carbon paper forms, that I am sure you fill out every day, you will pick up PCB's in analysis of those forms. We have run a scan on some of those at the laboratory. They are still pretty high. Some of them are older forms and quite often it is hard to date them. Some forms were produced before 1972 and are still around. This is one good source.

The other concern is that in some of the pigmented inks, back-documentation indicates the PCB's were used in formulation. This was documented in the departmental task force presentation on PCB's. I believe there are patent numbers associated with this documentation.

We are still working on inks, taking a cross section. I would like to know that PCB's are not there, because if they are used in inks, we have a real problem, and the paper recycling industry has a real problem.

MR. BEGGS: Thank you.

MR. FRANK DICK (Converters Ink Company, Linden, New Jersey): The gentleman from New Jersey, my contact, Doctor Seymour Gilbert in the Food Science Department at Rutgers University, probably has a bigger file on PCB's than anybody in the country.

MR. BREMER: Fine. Thank you.

MR. THEOPHILUS R. CARSON (Food and Drug Administration, Washington, D.C.): There are certain things that I cannot say. But I can say that our chemists have been working on the methods of determining PCB's. And if I can get your name, I might be able to get you some information that could help you.

RECOVERY OF MATERIALS USED IN LETTERPRESS AND ROTOGRAVURE PLATE PREPARATION

William A. Rocap, Jr.*

Abstract

The materials used in the construction of letterpress and rotogravure printing plates are identified, and the handling of them is discussed, with particular attention to their recovery and recycling. The chemicals used in plate preparation as well as in the preparation of the materials used in the "prep" areas are also discussed, with like emphasis on the ability to recover recycle, or reuse. The overall theme is to discuss the above with respect to the impact of platemaking operations upon the environment. Slides will be shown to illustrate the presentation.

Before proceeding to the identification of specific materials and processes in the letterpress and rotogravure segments of the graphic reproduction industry and looking at their impact on the environment, I would like to make a few observations concerning the approach which is being taken to these matters from several viewpoints.

First of all, I would like to commend the people who have put this program together on their choice of a title "Conference on Environmental Aspects of Chemical Use in Printing Operations." During the past several years, it has been the practice to brand many of the people who have been involved in the printing and related industries as pollutors of every part of the environment whether or not this has been, in fact, true. Much of the finger pointing and damaging adverse publicity has been spawned by people who care very little about either our business or our government and would, in fact, like to bring both down. Unfortunately, at times, the press in an effort to capture sensational headlines and some do-gooders who really do not know the first thing about the problems being discussed, join in. This may be news to some of you but let me please tell one brief story to illustrate my point. A series of announcements were run about a year ago on

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*Director of Research and Development, Meredith Printing, Division of Meredith Corporation, Des Moines, Iowa.

radio and T.V. telling their listeners of the evils of pollution. They appealed for action on the part of the citizen: "If you see smoke coming from a stack, report it," etc. This was followed up by many articles in local papers along the same line.

About a week after this general attack on industry, a class of junior high students toured one of the local plants. One little boy firmly told his tour guide, "We are going to shut this plant down." You see, the propaganda had hit the mark. My question is, is this the way to solve our environmental problems?

A second observation involves semantics again. Many plants have what they call a quality control department. Some plants prefer to call this a quality measurement or quality assurance department; why? It is felt that the people who are directly responsible to the management, owners, and stockholders for the quality of the product are the ones who should be controlling the process. I read in a trade publication recently, "So the question is, does the government want to control pollution or control industry? If the objective is to lessen pollution quickly and dramatically, requiring less would accomplish more." Again, I like the title Environmental Protection Agency better than Environmental Control Agency, and it would behoove all of us to strive to keep EPA protecting rather than controlling.

My third point is one of procedure and it involves the way many of our larger companies have already set up within the framework of their staffs one person or more responsible for environmental impact.

There is much to concern the printer today other than producing graphic reproduction on time, with acceptable quality and hopefully at a profit. He must now face the problems posed by a myriad of Federal, State and local laws, regulations, and programs. He has to deal not only with environmental problems concerning air, water and solid waste, but with OSHA, fair employment practices, equal rights, and a myriad of other regulations, the existence of which he has not the slightest knowledge.

The printing industry is a very large one and it employs a vast army of people; however, many of the graphic reproduction establishments are quite small, with 20 employees or less. One large printing plant with which I am acquainted has three people who work full time on problems related to the environment. Much of this time is spent in reading the new regulations that come out in a seemingly endless stream, week after week, and in trying to interpret them to their own situation. In a small plant, the plant manager must add this function to an already busy schedule. Is it any wonder why in many cases he simply does not know of the regulations or how they apply to his situation? Recently a technical representative of a fairly large supplier of graphic reproduction material tossed a copy of a technical bulletin on standards for photographic effluents on my desk, with the question, "What is this all about? I can't make heads nor tails of it?" This from a graduate chemist who has been in the trade a number of years. My third suggestion then is to "keep it simple." Because of the nature of our graphic reproduction industry, new laws and regulations should be widely disseminated in understandable language. Trade associations and trade publications should be in the vanguard to accomplish this.

I. I would like to first mention the materials used in the preparation of letterpress plates and rotogravure plates and cylinders. In the preparation of letterpress plates, it is necessary to produce relief type and halftone images on some sort of image carrier or plate from which this image is transferred to a substrate such as paper, plastic, etc.

   1. In order to produce the halftone images or illustrations, it is generally necessary to produce continuous tone and line film from which a sensitized plate in imaged. The production of this film involves photographic processing that generates photographic wastes. Here I would like to quote PERI Information Bulletin No. 14 (ref. 1) on this item. "Manufacturers of photographic materials have generally given a great deal of attention to the problems of waste disposal and their technical personnel can generally aid the platemakers in such matters."
   2. The Eastman Kodak Company has an excellent publication called "Disposal of Photographic Processing Wastes" (ref. 2), which should be in every platemaker's library. One metallic element found in wastes of all common photographic operations is silver, which is present in used processing baths as a silver-thiosulphate complex. Both from the economic standpoint as well

as for environmental control, it is important that this metal be removed and recovered. Excellent silver recovery systems are available through graphic arts suppliers. They remove silver from solution either by electroplating the metal onto a metal cathode, or by a chemical reaction that causes it to deposit on metallic fibres. All platemakers should consider such treatment, both because silver recovery helps to insure a continuing supply of a metal vital to the platemaking industry and because it is a means of environmental protection.

3. One recent development in the area of film is the Scott S.G. film which is silverless and does not require a development solution for processing. It is processed by ammonia, which of course requires a somewhat different environmental treatment.
4. Another recent development in film is the 3M QA Mark IV graphic film, which is advertised for the "elimination of all high polluting substances from coatings on both sides of the film."
5. Insofar as reclaiming of used and scrap film is concerned, it is collected in drums and sold for approximately 30¢ per lb.
6. One source of original halftone material for letterpress is the making of copper engravings. This is done by carefully cleaning and sensitizing the copper surface after which the image is contact-exposed or "burned" into the sensitizing resist with a powerful light source. The unexposed resist is developed or washed away with warm water and the remaining resist is hardened by heating. The imaged plate is now engraved by treating with a ferric chloride solution in an etching machine. The waste etchant contains ferric chloride and dissolved copper along with several organic additions. Unfortunately, there is insufficient copper involved to make it feasible to reclaim so the used etching solution is treated in tanks made of polyvinyl chloride, polyethylene, or other material which resists attack by ferric chloride. It is preferable to dilute the used etching bath with 1 and 2 volumes of water before adding the neutralizing material. The preferred neutralizing chemical for ferric chloride baths is sodium hydroxide and for ease of handling a 50 percent solution is recommended. As

neutralization takes place, a heavy brown precipitate of iron compounds will form. When formation of the precipitate ceases, neutralization is complete. After the precipitate has settled, the clear solution is drained off and is further treated with limestone and sent to the sewer. The precipitate is dried, made into cakes and is hauled off, usually by a paid disposal service. The used plates are sold as scrap as are the trimmings and shavings, the copper being kept separate from other metals during processing.

7. Zinc and magnesium are used in addition to copper engravings, as original etched plates in the letterpress process. Like copper, the sheet magnesium and zinc etching baths must be treated in order to dispose of them properly. Also like copper, the zinc and magnesium metal is carefully separated and returned to a metals dealer for recycling. A number of firms assemble and sell packaged units for the treatment of etching wastes. Among these is the Ball Metal and Chemical Company, Greenville, Tennessee, which handles a unit that can be modified to handle products of zinc, magnesium, and copper etching.

8. Type metal consisting of 82 percent lead, 11.5 percent antimony, and 6.5 percent tin is used in linotype, monotype, and foundry type setting for the manufacture of letterpress plates. Most of this material can be very readily recycled and is exchanged pound for pound with the payment of a very small refining fee.

9. Rotogravure prepress operations use film in the same manner as letterpress preparation, with one additional step--the preparation of carbon tissue used to control the delicate etching of the tiny cells into the gravure copper. There is also the plating of the rotogravure cylinder with copper and its washing and polishing, which necessitates treatments of these rinses to remove the copper. After use, the gravure cylinders are stripped of their Ballard shells of the plated copper. The shells are dechromed with HCl and are sold as an almost pure copper; however, they do contain a trace of nickel from the "parting layer" of the gravure cylinder.

A recent development in rotogravure called mechanical engraving, which is done with a machine called a Helio-Klischograph, eliminates the need for an etching step in producing the ink-carrying cells on the cylinder. However, much liquid etching with ferric chloride is still done, and this etching bath, must be treated and disposed of in the same manner as the letterpress copper engraving bath. Unfortunately, an economically feasible method of reclaiming the copper from this bath has not been found. In the case of the rotogravure cylinder, after etching, proofing, and correcting, it is chrome plated and used directly on the rotogravure press.

II. In the letterpress process, original engravings and set-type are rarely used in the actual printing processes. Rotary printing presses require curved plates and one such duplicate plate is the electrotype. In electroforming an electrotype, a plastic mold is made of the original engraving and type by pressing a sheet of pure plastic against the form under carefully controlled heat and pressure. (It should be possible to find a use for this molding plastic, which is thermoplastic, but unfortunately it is presently scrapped.) After molding, the plastic is sprayed with silver to make it conductive, the excess silver spray being carefully collected and recycled. The silvered plastic is electroplated with nickel, copper, tin, and finally chrome to give it a long-wear characteristic. The shell thus produced is an exact replica of the original engraving and type and it is curve cast in a rotating cylinder, forming a curved press plate by a process called centrifugal casting. After shaving and correcting, this curved segment is finished and is delivered to the pressroom. After its run in the pressroom, the discarded plate is separated mechanically and the elements are returned to a metals refiner where they are exchanged pound for pound. A small price is paid for the refining. Time does not permit going into detail to describe the care necessary in handling the plating baths. Great care, though, is exercised in employing as much of the used materials as possible. Copper, for example, is recovered from the copper bath electrolytically, as is the chrome. The used copper anodes, nuggets, etc., are returned to the metal supplier and are recycled.

Stereotypes are also duplicate plates that are made from originals by "rolling up a matte" and casting molten type metal into the matte in a curved casting mold. Stereotypes are largely used to produce newspapers and since they are made entirely of type metal, they can be very readily recycled and reused, usually onsite.

III. In the past several years, a number of plastic letterpress plates have found widespread use, particularly in newspaper printing. Typical brand names are NAPP, Dycril, Kodak KPR, Brace, Merigraph, etc. These plates are made of various plastics, usually polymers--polyamindes, polyurethane, etc.--and they consist of the imaged plastic usually attached to a thin sheet of aluminum. The aluminum bases can be recycled, but the plastic polymers cannot. The plates are made by several means, from both solid and liquid materials, but generally an exposure to light through a negative and a washout to produce the relief is necessary. Some of the washed out plastics are biodegradable and are washed out with warm water and run down the sewer; others are insoluble and are collected, treated, and disposed of in sanitary landfills, etc.

IV. One important development similar in some respects to the mechanical engraving of the rotogravure cylinder--which eliminates many steps, including liquid etching and its associated disposal problems--is the laser-etched letterpress plate. This is produced by engraving a letterpress plate through scanning a black and white line copy with a laser and producing an engraved plate by removal of plastic with two other lasers. Control of the vaporized plastics is of course necessary but liquid echants are eliminated.

In conclusion, it might be said that much has been done to reclaim and recycle the materials used to make letterpress plates and rotogravure cylinders, but there is still much to be accomplished. The future looks exciting though challenging.

(The following 9 figures are illustrations of the processes described in this paper.)

Figure 1. Conservation of water by use of recirculators such as this one used in color film processing, resulting in savings of water and heat.

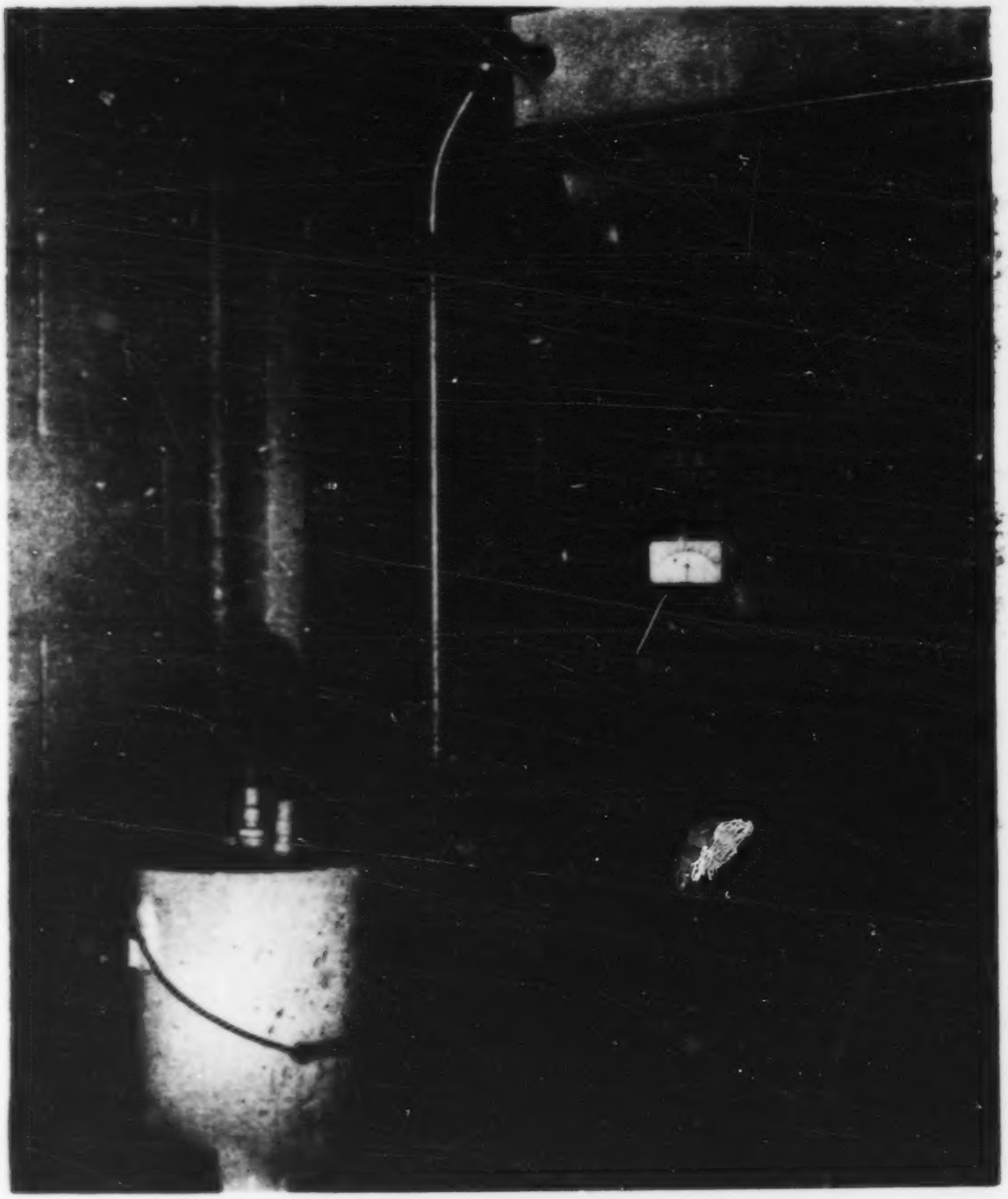

Figure 2. Silver reclaim unit on each photographic film processor to recover silver.

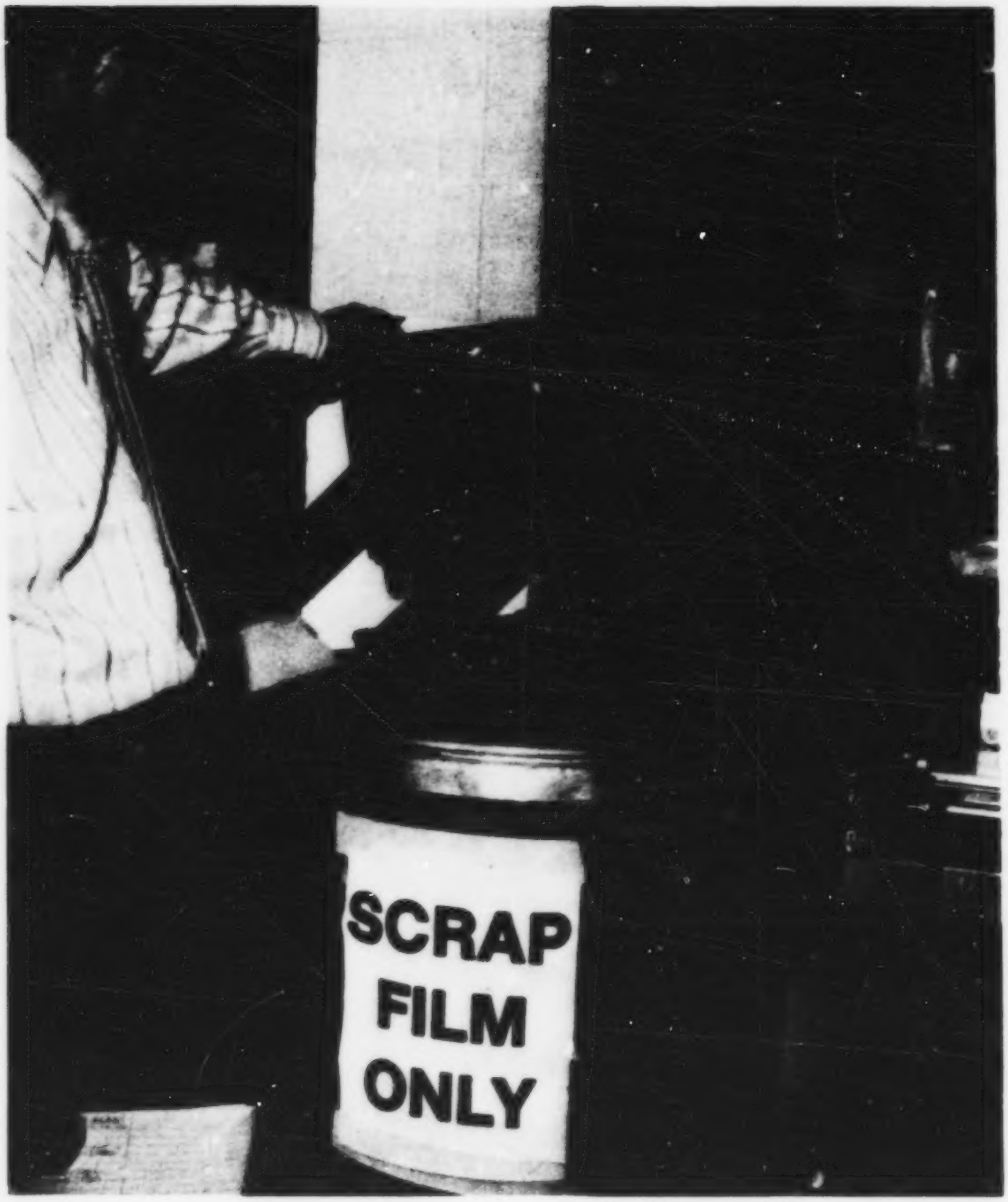
SCRAP
FILM
ONLY

Figure 3. Collection of film in drums to be sent to a reprocessor for recovery of silver and other materials.

Figure 4. Copper recovery unit to remove copper from concentrated plating solution; it recycles both the copper and the bath.

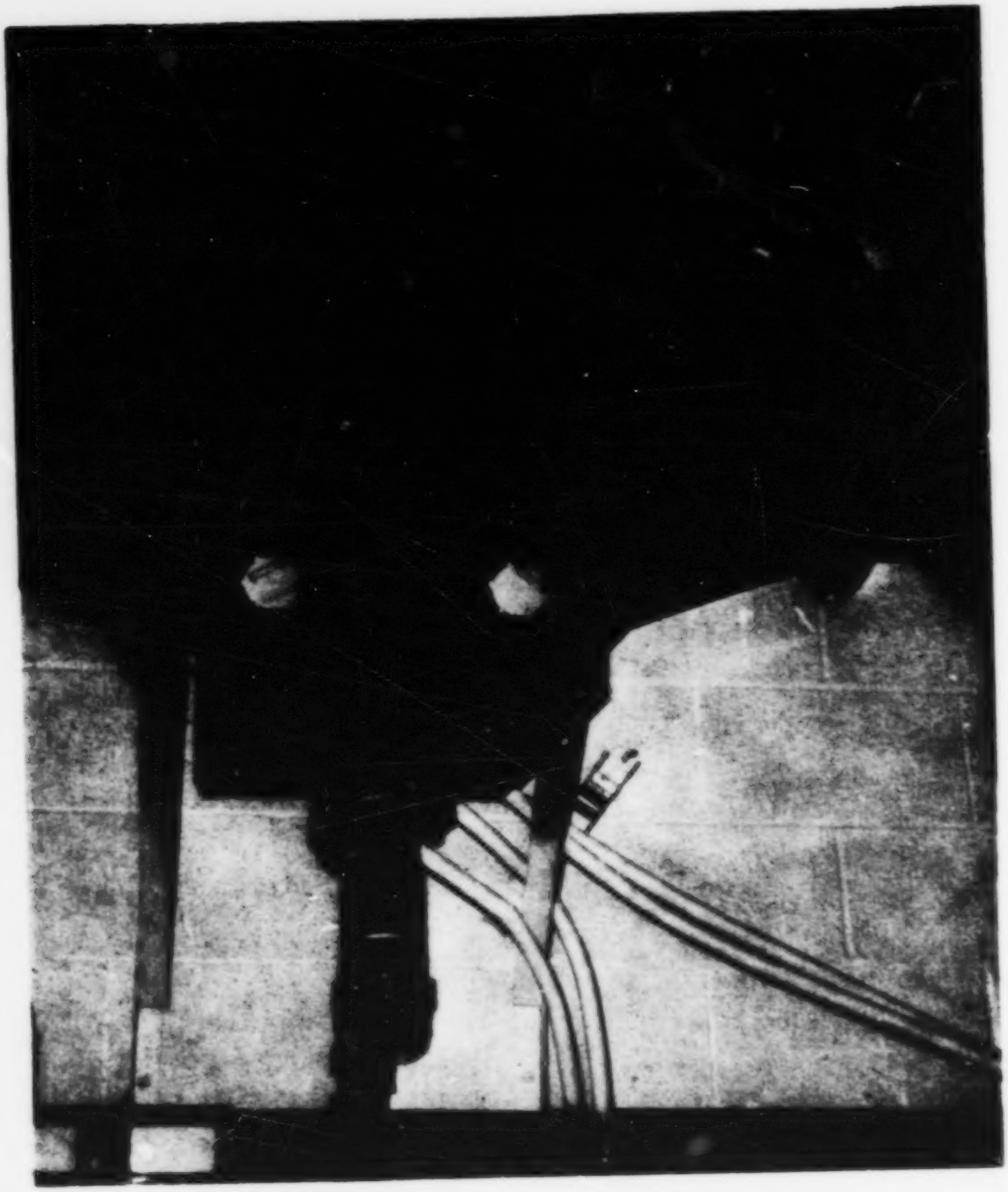

Figure 5. Fume separator over the copper recovery unit to filter out and recover any carried-over materials.

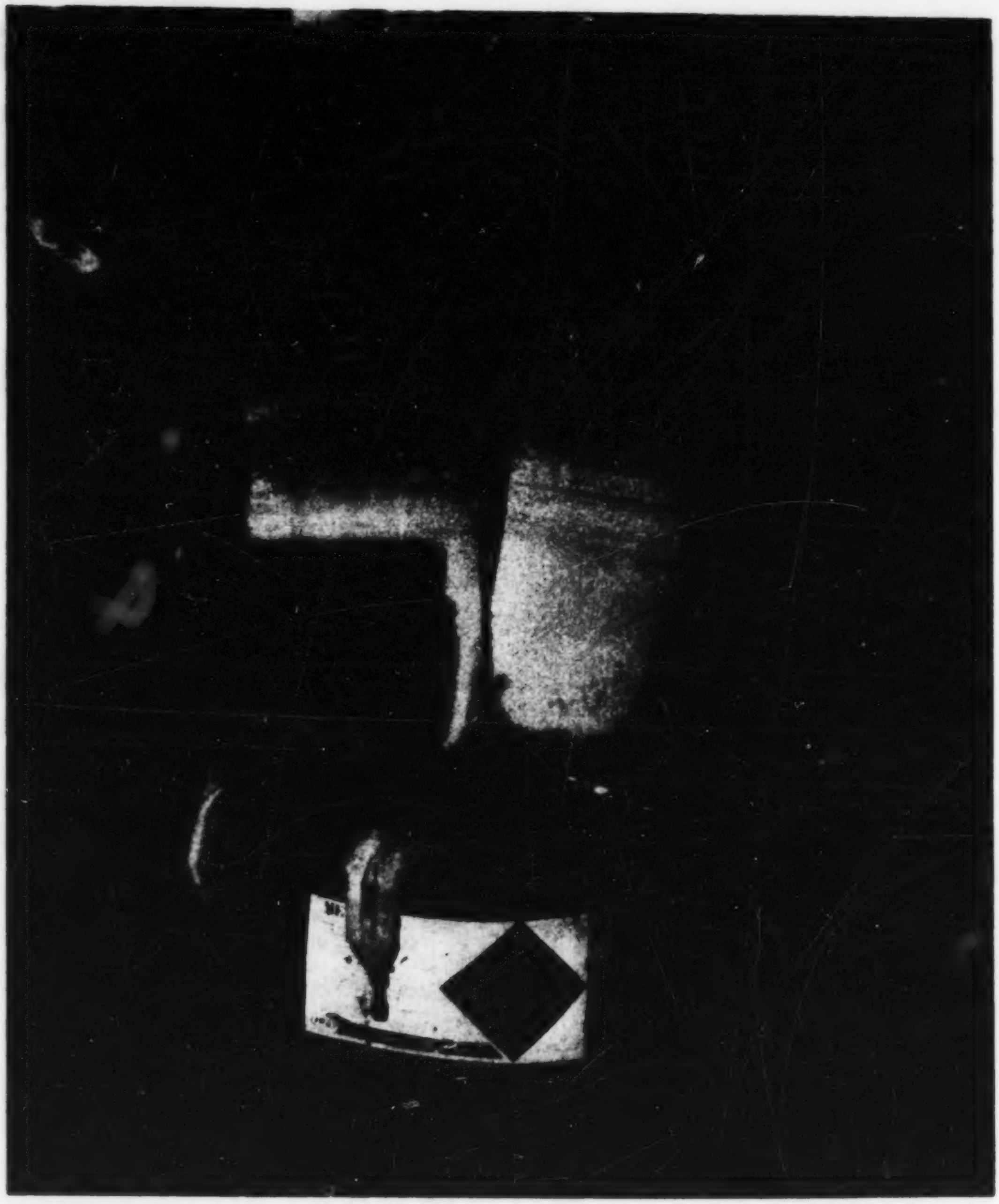

Figure 6. Copper anodes sent out to be recycled are made into new anodes--replaced pound-for-pound with a small recycling charge.

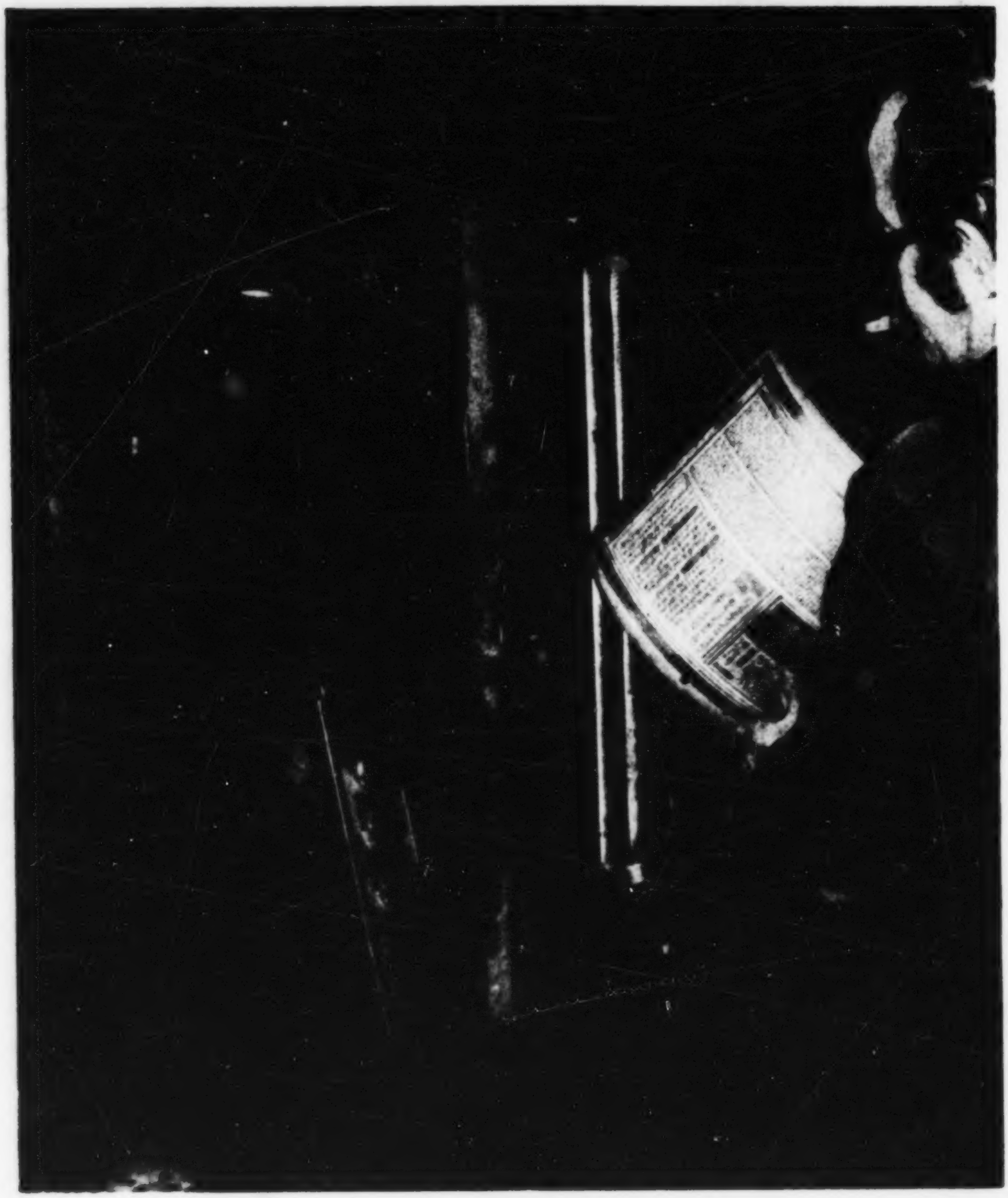

Figure 7. Machine used to separate the various metals of the letterpress plates for more advantageous recycling.

Figure 8. Used monotype and linotype metal ready for return to the foundry to be recycled.

Figure 9. View of plate materials that have been separated and are ready to be sent to a metals converter to be recycled.

REFERENCES

1. Pollution and the Platemaker, PERI Information Bulletin No. 14, Photoplatemakers Educational and Research Institute, Park Forest, Illinois, January 1971.

2. Disposal of Photographic Processing Wastes, Publication No. J-28, The Eastman Kodak Company, Department 412-L, Rochester, New York.

SOLVENT RECOVERY IN A MODERN ROTOGRAVURE PRINTING PLANT

B. Gordon Watkins, Jr., and Paul Marnell, Eng. D.*

Abstract

Toluol, the principal solvent in rotogravure inks, is the common name for the aromatic hydrocarbon methylbenzene ($C_6H_5CH_3$). Toluol is a photochemically reactive organic compound which reacts with oxidizing chemicals in the atmosphere under the influence of sunlight to form what is commonly called "smog." Progressive management stipulated that the new Meredith/Burda rotogravure printing plant to be built in Lynchburg, Virginia, should be as pollution-free as modern technology could provide. A fully automatic solvent recovery system captures toluol vapors at their sources on the printing presses and recovers liquid toluol, which is reused in making gravure ink at the nearby ink plant. This paper illustrates the basic components of the solvent recovery system and describes their operation. Design objectives and operating performance of the system are presented.

In late 1969, Meredith Corporation of Des Moines, Iowa, joined forces with Burda Druck GmbH, headquartered in Offenburg, West Germany, to form Meredith/Burda, Inc. The goal of this venture was the construction and operation of a modern and highly efficient rotogravure printing plant, which would utilize the best technology of both parent companies. A site was selected in Lynchburg, Virginia, and construction of the 120,000-square-foot first stage of the plant began in 1970. An additional 115,000 square feet were placed in operation in mid-1974.

Progressive management dictated that the new plant would not only produce the highest quality product, but would be as pollution free as could be designed. It was imperative that Meredith/Burda be a good neighbor in its beautiful setting on a hill in suburban Lynchburg. This policy meant in practical terms designing a plant with extremely low levels of air and water pollution and odor emission. This paper presents the system used to control the emissions of the vapor of the principal solvent in rotogravure ink, toluol.

Toluol is the common name for the aromatic hydrocarbon methylbenzene ($C_6H_5CH_3$). It is a highly flammable, moderately volatile, moderately toxic liquid. In vapor form toluol is considered an air pollutant. As a photochemically reactive organic compound, it reacts with oxidizing chemicals in the atmosphere under the influence of sunlight to produce what is commonly known as "smog."

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*B. Gordon Watkins, Jr., Vice President and Manager of Project Administration, Wiley & Wilson, Inc., Lynchburg, Virginia; Paul Marnell, Manager, Environmental Business Development, American Lurgi, Inc., Hasbrouck, New Jersey.

The Regulations for the Control and Abatement of Air Pollution of the Commonwealth of Virginia (ref. 1) provide specific limitations on the amount of organic solvents that may be lawfully emitted to the atmosphere. Paragraph 4.05.03 (g) of these regulations, entitled "Organic Solvents," states: "A person shall not discharge more than 40 pounds of organic material into the atmosphere in any one day from any article, machine, equipment, or other contrivance used . . . for employing, applying, evaporating, or drying any photochemically reactive organic compound or material containing such solvent unless all organic materials discharged from such article, machine, equipment or other contrivance have been reduced by at least 85% overall . . . . Emissions of organic materials into the atmosphere . . . shall be reduced by:

(a) Incineration

(b) Adsorption, or

(c) Processing in a manner determined by the Board to be not less effective than (a) or (b) above . . . . The word person shall be synonymous with and have the same meaning as the word owner . . . ."

In order to comply with these regulations as a minimum requirement, a solvent recovery system having two basic objectives was designed for the plant:

1. Solvent removal from the exhaust-air from the printing press dryers, which would meet and exceed any existing air pollution, health, or safety ordinances regulating emissions of toluol vapor into the atmosphere;
2. Recovery of liquid toluol of sufficient quality and in sufficient quantity to be economically worthwhile to use in the manufacture of gravure inks in the nearby ink plant.

The solvent recovery system selected for use at the Meredith/Burda plant in Lynchburg was designed by Lurgi GmbH of Frankfurt, West Germany, and installed under the direction of American Lurgi, Inc. Installation was designed by the firm of Wiley & Wilson, Inc., Engineers-Architects-Planners, headquartered in Lynchburg, Virginia. This presentation will describe the specific Lurgi system installed in the Meredith/Burda plant, although certain principles are common to other solvent recovery systems.

The basic system consists of four principal elements: collection of vapors, transporting vapors to the solvent recovery plant, adsorbing the vapors, and finally condensing and separating the liquid toluol. Although oversimplified, figure 1 illustrates the concept of the complete system.

Toluol begins to evaporate from the web immediately after being in contact with the impression cylinder. Most of the vapor is captured and drawn into the dryer at point ① (figure 1). Other escaping toluol vapors from the web and ink fountain settle to the floor, since toluol has a vapor density relative to air of 3.1, and are collected by the floor sweep (point ②).

The presses installed at Meredith/Burda utilize a steam-heated, recirculating forced air dryer on each unit to vaporize the solvent from the web. A portion of the recirculated air, approximately 2,000 cubic feet of air per minute per unit, is continuously drawn off for transport to the solvent recovery plant (point ③, figure 1).

The uptake duct from the dryer on each unit of the press (figure 2) includes a paper filter, motor-operated shutoff valve, which is connected to the dryer blower motor, and a flow indicator with an alarm.

A uniform flow of air and vapor from each press to the solvent recovery plant is kept uniform by a motor-operated valve, which maintains a constant 150 mm H_2O negative pressure in the press header duct (item ④, figure 1).

The solvent recovery plant serves four 10-unit rotogravure presses and one four-unit proof press. The common transport duct is run above the roof (item ⑤, figure 1). It is protected from fire internally by an automatic carbon dioxide deluge-type system. The duct is equipped with lightning rods to reduce the chance of damage from this source. The duct contains a solvent concentration meter, which will sound an alarm in the pressrooms if the toluol vapor in the duct reaches 25 percent of the lower explosion limit and will shut down the presses automatically if the concentration should reach 40 percent of the lower explosion limit.

The recovery plant itself consists of filter house, blowers, adsorbers, condenser-aftercooler, and separator.

The filter house (item ⑥, figure 1) contains a traveling curtain, self-cleaning air filter. Five direct-drive high pressure blowers (item ⑦) operating in parallel provide the total motive force to move the air-vapor mixture from printing-press dryer systems to the discharge side of the adsorbers. Six identical adsorber tanks (item ⑧) cleanse the air stream of solvents. The

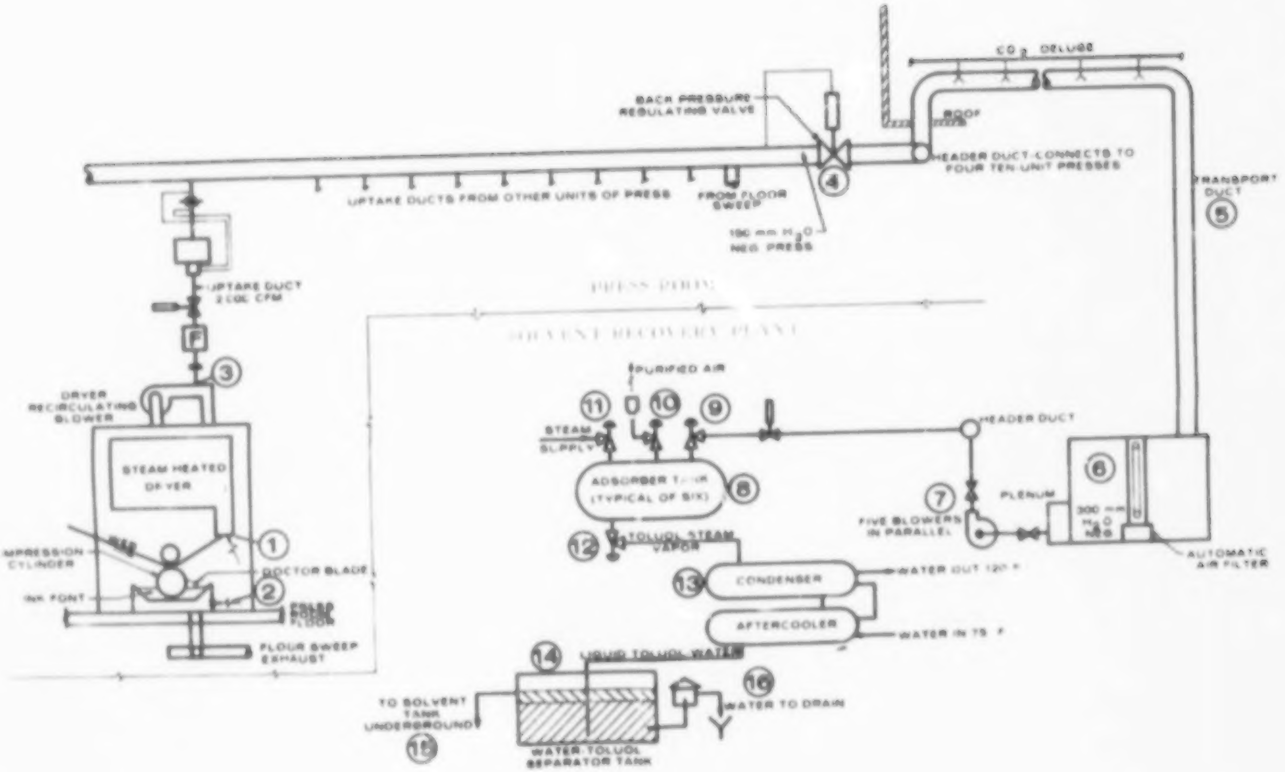
BACK PRESSURE REGULATING VALVE
ROOF
CO2 DELUGE
HEADER DUCT-CONNECTS TO FOUR TEN-UNIT PRESSES
TRANSPORT DUCT
5
4
UPTAKE DUCTS FROM OTHER UNITS OF PRESS
FROM FLOOR SWEEP
190 mm H2O NEG PRESS
UPTAKE DUCT 2 COC CFM
F
3
PRESS ROOM
SOLVENT RECOVERY PLANT
DRYER RECIRCULATING BLOWER
STEAM HEATED DRYER
1
MPRESSION CYLINDER
DOCTOR BLADE
2
INK FONT
PRESS FLOOR
FLOUR SWEEP EXHAUST
PURIFIED AIR
11
10
9
STEAM SUPPLY
HEADER DUCT
ADSORBER TANK (TYPICAL OF SIX)
8
6
7
PLENUM
FIVE BLOWERS IN PARALLEL
300 mm H2O NEG
AUTOMATIC AIR FILTER
12
TOLUOL STEAM VAPOR
13
CONDENSER
WATER OUT 120 F
AFTERCOOLER
WATER IN 75 F
14
LIQUID TOLUOL-WATER
16
WATER TO DRAIN
TO SOLVENT TANK UNDERGROUND
15
WATER-TOLUOL SEPARATOR TANK

Figure 1. Schematic of the solvent recovery system.

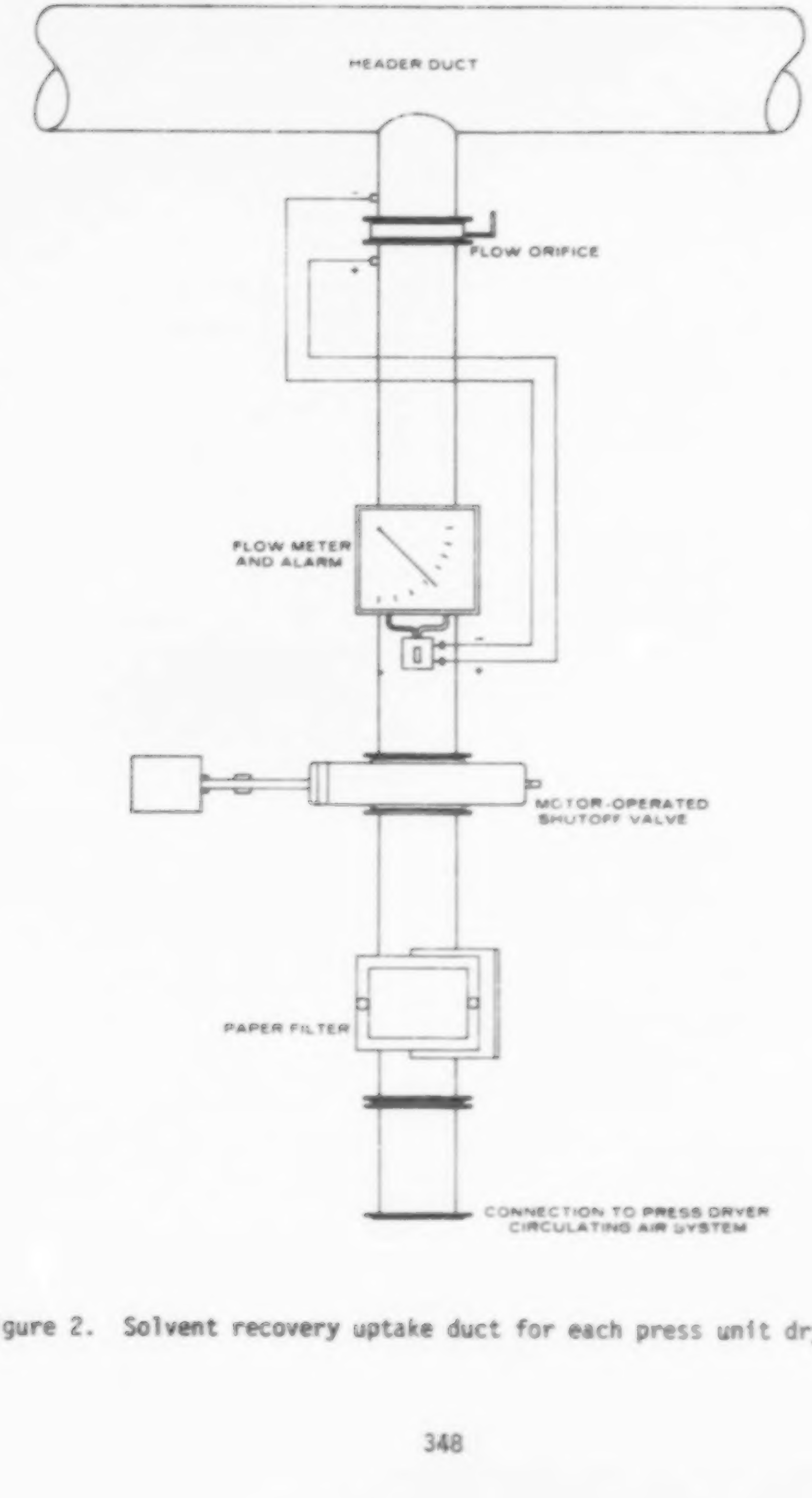
HEADER DUCT
FLOW ORIFICE
FLOW METER AND ALARM
MOTOR-OPERATED SHUTOFF VALVE
PAPER FILTER
CONNECTION TO PRESS DRYER CIRCULATING AIR SYSTEM

Figure 2. Solvent recovery uptake duct for each press unit dryer.

fully automatic control system maintains five adsorbers on the line at any one time with the sixth unit being regenerated. Each adsorber tank contains a bed of activated carbon held in place by ceramic grilles.

During normal operation of the adsorber tank, inlet valve ⑨ (figure 1) is open and the air-vapor mixture is circulated through carbon beds. Cleansed air is discharged to the atmosphere through valve ⑩. During regeneration, valves ⑨ and ⑩ close, and steam is admitted through valve ⑪, steaming the adsorbed vapor from the carbon. The toluol-steam mixture passes through valve ⑫ and is condensed and cooled in the condenser-aftercooler ⑬. Finally the water and solvent are separated by specific gravity in tank ⑭. The liquid toluol is piped to an underground storage tank ⑮ and water is discharged to drain ⑯.

The method utilized to provide cooling water for the condenser-aftercooler is worthy of special mention. The criteria for cooling water dictated by design of the condenser-aftercooler required that the water entering the aftercooler be a constant 75° F all year. A normal full-load water temperature leaving the aftercooler would be 120° F. The required entering water temperature was too low to utilize a cooling tower in summer, and city water would be expensive. To cool the water entirely by mechanical refrigeration would also be expensive. A further consideration was the desire of the engineers to use a closed-circuit water loop for the condenser-aftercooler to eliminate regular shutdowns for cleaning the tubes of these heat exchangers.

The equipment and piping system selected by the engineers to provide the cooling water is illustrated graphically in figure 3.

Primary and secondary pumping circuits are utilized, with most cooling of the water being done by a Fluid Cooler (item ①, figure 3). Water leaves the condenser-aftercooler (item ②) at 120° F and enters the coils of the fluid cooler. A fluid cooler is similar to a cooling tower except that the water to be cooled flows through closed coils while recirculated water is sprayed over the coils, cooling the water in the coils by evaporation.

At normal maximum summer-design conditions water will be cooled by the fluid cooler from 120° F to 85° F. A portion of this 85° F water is returned to the plant chilled-water-system return main (point ③, figure 3). The plant chilled-water supply ⑤, which is 42° F, is blended with the 85° F return water to produce 75° F water to the condenser-aftercooler unit (point ⑥). As outdoor temperature and humidity drop, the temperature of water leaving the fluid cooler drops. When the temperature drops to 75° F, no plant chilled water is required, and the water is cooled exclusively by the fluid cooler. Water temperature in

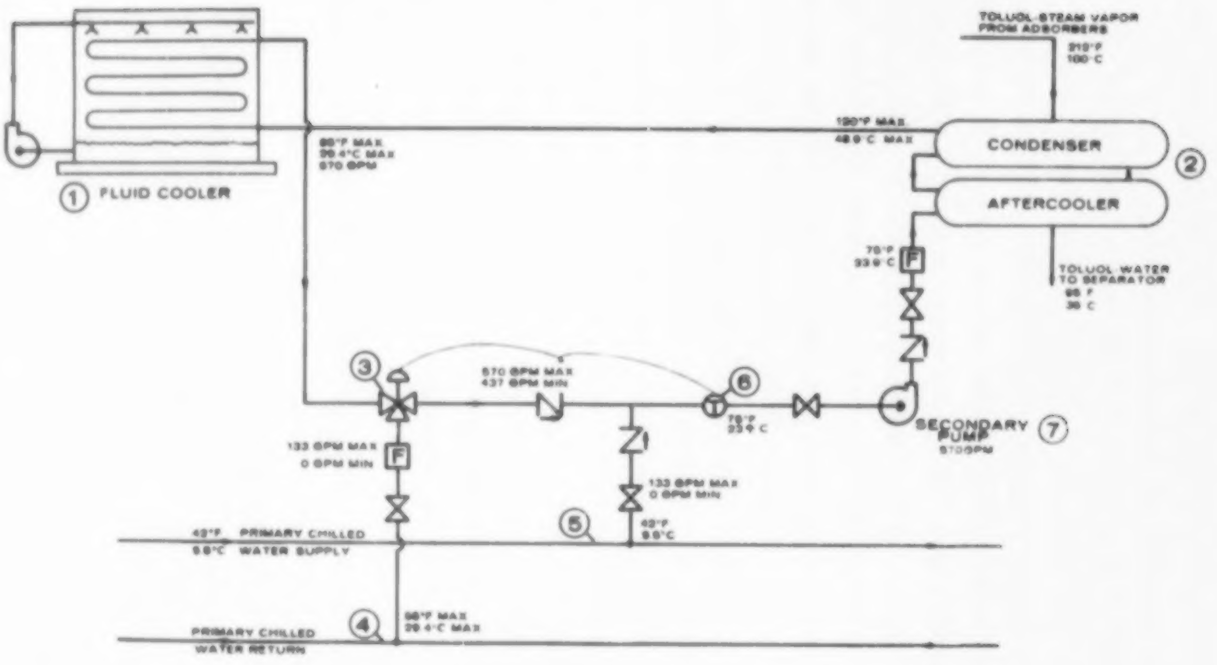
TOLUOL-STEAM VAPOR FROM ADSORBERS
212°F
100°C
120°F MAX
48.9°C MAX
CONDENSER
AFTERCOOLER
②
TOLUOL WATER TO SEPARATOR
86°F
30°C
75°F
23.9°C
① FLUID COOLER
85°F MAX
29.4°C MAX
570 GPM
③
570 GPM MAX
437 GPM MIN
⑥
75°F
23.9°C
SECONDARY PUMP
570GPM
⑦
133 GPM MAX
0 GPM MIN
F
133 GPM MAX
0 GPM MIN
42°F
5.6°C
⑤
42°F PRIMARY CHILLED
5.6°C WATER SUPPLY
④
85°F MAX
29.4°C MAX
PRIMARY CHILLED
WATER RETURN

Figure 3. Schematic of pipe solvent condensing.

cold weather is maintained at 75° F by sequential control of fans and damper control on the fluid cooler. This sytem has demonstrated a significant saving in energy while maintaining the reliability of the system.

The process aspects and the economics of the solvent recovery plant are presented in the following paragraphs.

The Lurgi Supersorbon* process is employed universally for the recovery of various organic solvent vapors and contributes, therefore, to increasing the profitability of many industrial operations. At the same time, it prevents the discharge of noxious vapors into the environment, and its use brings about compliance with the air pollution acts brought into force in recent years. At present, there are over 3,000 Lurgi Supersorbon plants in operation worldwide.

The Supersorbon process, which is based on the affinity of certain activated carbons for organic vapors, can be applied in most industries employing solvent, e.g., surface coating, impregnating, extracting, rotogravure, viscose fibres, acetate silk, films, rubber goods, imitation leather, etc. In this paper, we describe its utilization in a modern rotogravure plant. However, the principles are quite general and are employed in most applications of the process.

The Supersorbon process comprises two key steps:

1. The purification of the solvent-laden exhaust-air (SLA) by exposure to Supersorbon activated carbon, which results in a selective and highly efficient adsorption of organic vapours, even at low concentrations. The removal efficiency generally exceeds 99 percent.
2. The regeneration of the carbon, with steam permitting the recovery of the adsorbed solvents and the further solvent recovery by the carbon.

Properties of the Adsorbent

Before describing the sequence of process steps, it is worth while to mention the characteristics of the activated carbon used to remove, by adsorption†, the printing ink solvents from the SLA (solvent-laden exhaust air).

Activated carbon is a product of organic matter (e.g., peat, wood, brown coal, coconut shells), which is produced in numerous special grades. For exhaust air purification and solvent recovery, cylindrical shapes with a grain size of 3 to 4 mm and a bulk weight of approximately 380 kg/m^3 are used. Depending on the application, a grade is selected having suitable capillary structure, surface area, adsorptive capacity, and mechanical strength. The inner surface area of the various grades is in the range of 1,000 to 1,500 m^2/g of activated carbon.

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*Supersorbon is a registered trademark of Lurgi.

†Consult any standard physical chemistry text for a discussion of the adsorption mechanism. For our purposes here, we may describe it as a purely physical process whereby the surface forces of the carbon are such that the solvent vapor molecules are bound to the carbon surface. As the temperature is increased, the bound vapor molecules are further energized and can overcome the binding forces and thereby escape (desorb).

The key point is that the carbon used should be tailored to the application. This will insure maximum recovery at a minimum cost.

We will now describe the two key process steps, i.e., adsorption and desorption (regeneration).

Adsorption (Charging Cycle)

The solvent-laden air (SLA) produced at the rotogravure machines is drawn off by means of the blowers and, after dust removal, flows upward through a portion of the adsorbers. The other adsorbers are simultaneously being regenerated, i.e., the solvent is being removed for them. The adsorbers are filled with the highly activated Supersorbon carbon, which is supported on perforated ceramic trays, which in turn are supported on grates. The activated carbon adsorbs the solvent, and the solvent-free air leaves through the top of the adsorbers to the atmosphere.

The adsorber-charging step is continued until the solvent is no longer completely adsorbed in the uppermost activated carbon layers. This so-called "breakthrough" (end of charging cycle) is monitored by a concentration-measuring instrument called a Solvomat* installed in the switch panel, which serves to initiate automatic control of the Supersorbon plant.

Desorption (Regeneration)

When breakthrough occurs, the gas inlet and outlet valves ⑨ and ⑩ (figure 1) to the adsorbers are automatically (by means of the Solvomat signal) closed and the steam inlet and distillate valves ⑪ and ⑫ are opened. The object of the steaming process is to raise the temperature of the carbon bed in order to free the bound solvent molecules from the surface of the Supersorbon activated carbon. The slightly superheated steam passes down through the bed, and the resulting steam-vapor mixture leaves the bottom of the adsorber and is condensed in a condensor-aftercooler unit ⑬.

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*Solvomat is a registered trademark of Lurgi.

Since toluene and water are immiscible, the toluene is easily recovered in the separator and then sent to tank storage.

After desorption, the hot and moist Supersorbon carbon in the adsorber is dried and cooled down to normal charging temperature as quickly as possible. This drying and cooling of the activated carbon is achieved by recharging with SLA. For this mode of operation, it is essential that the activated Supersorbon carbon has a sufficiently high adsorptive capacity even at elevated temperatures.

The Meredith/Burda plant is fully automatic, so that the timed sequencing of the charging and regeneration of each adsorber is controlled by instrumentation. The Solvomat concentration analyzer developed by Lurgi monitors the exhaust vapor solvent concentration. When the concentration rises, the Solvomat transmits a control signal whereby the inlet and outlet air valves ⑨ and ⑩ are closed, and immediately thereafter (2 to 3 seconds) the steam and distillate values ⑪ and ⑫ open to initiate the regeneration step. In general, an adequate number of adsorbers must be available to handle the solvent removal while the other adsorbers are regenerated. At Meredith/Burda, five adsorbers are in various stages of charging while one adsorber is discharging (being regenerated).

Maintenance of the Supersorbon plant is routine and is carried out during the period set aside for press maintenance. Hence, the Supersorbon solvent recovery plant does not reduce or curtail production time in any way.

The original carbon charged in 1971 is still performing satisfactorily with no apparent need for recharging imminent.

The general economic operating parameters of a Supersorbon plant are stated below:

Operators per Shift	1
Utilities	
Steam (25 50 psi), lb steam/lb recovered solvent	2-3.5
Electricity, kWh/lb recovered solvent	0.1
Cooling Water, gal/lb recovered solvent	4 6
Carbon Loss, lb carbon/lb recovered solvent	0.0005 0.001

The basic operating data for the Lurgi Supersorbon facility at Meredith/Burda are as follows:

OPERATING DATA

Operating days per year	250
Shifts per day	3

Throughput of solvent-laden air	88,000 cfm
Toluol recovery per 24-hour day	6,720 gal
Electricity	13,000 kWh/day
Water (closed system cooling)	20,000 gal/day
Steam (60 psig)	168,000 lb/day
Labor, man/shift	0.2 man/shift

The annual operating costs for the plant are:

ANNUAL OPERATING COSTS

Labor (@ $10/hr total)		$ 12,000
Utilities		
Electricity (@ 2.2 cents/kWh)		$ 71,500
Steam		
Gas Fuel, 80%	$ 16,400	
Oil Fuel, 20%	$ 12,200	
		$ 28,600
Refrigeration of condenser water		$ 2,000
Water		
Fluid cooler makeup	$ 1,360	
Steam makeup	$ 2,090	
		$ 3,450
Taxes and insurance (@ 3% of capital investment)		$ 36,000
Maintenance (@ 1% of capital investment)		$ 12,000
Total annual operating costs		$165,660

The capital investment costs for the plant are:

CAPITAL INVESTMENT COSTS

Solvent recovery equipment (including instruments and Lurgi engineering)	$800,000
Erection of solvent recovery equipment	$ 40,000
Water system piping (installed)	$ 71,000
Steam piping (installed)	$ 8,000
Process building	$174,000
Foundations and pipe supports	$ 12,000
Chilled water system (incremental cost charged to solvent recovery plant)	$ 72,000
Nonprocess engineering fee	$ 17,000
	$ 1,194,000

The annual recovery of purchased toluol is 97,200 gallons per month x 12 months = 1,166,400 gallons. At a current price of $0.59 per gallon, this represents a saving of $688,176. In addition, there is a recovery of the toluol in the purchased printing ink. This toluol is sold to the ink manufacturer. The credit is 42,800 gallons per month x 12 months x $0.20 = $102,720. (Note that the total monthly recovery rate of toluol is 97,200 + 42,800 = 140,000 gallons.) The total annual credit for recovered toluol is $790,896.

The overall plant economics can now be summarized as follows:

Capital Investment	$ 1,194,000
Annual Toluol Credit	790,896
Annual Operating Costs	- 165,550
Annual Profit	$ 625,346

Hence, the payout period (neglecting interest) is

$$\frac{\$1,194,000}{\$625,346/\text{Year}} = 1.91 \text{ Years}$$

In summary, the solvent collection and recovery system serves the important functions of safely removing solvent vapors from the printing presses and transporting them to a plant which through adsorption cleanses the solvent from the air stream. It recovers liquid toluol in sufficient quantity and purity to make the system an attractive investment for the modern rotogravure printing plant.

REFERENCE

1. "Regulations for the Control and Abatement of Air Pollution," State Air Pollution Control Board, Commonwealth of Virginia, February 3, 1974.

DISCUSSION

MR. W. N. FINGLAND (International Paper Company, Clinton, Iowa): I have some questions. In recovering toluene by adsorption, are you not also picking up other solvents? And then subsequently, how do you separate them? Finally, do you have a constant mixture of toluene that you are using?

DR. MARNELL: To answer the latter, we do have a constant mixture of toluene.

In the first instance, again, this particular plant was a simple plant in that it had a constant mixture. Toluene was the basic component. And most important, the toluene was immiscible with the water.

In the more general cases that we have handled, you have a mixture of hydrocarbons and then you have added distillation steps. So you have a little more in the way of capital equipment. But there is no problem as far as effecting the separation.

MR. FINGLAND: In the event you have a mixture, then you can distill out?

DR. MARNELL: Yes, absolutely. We have done this also.

MR. FINGLAND: Thank you.

MR. WILLIAM S. BEGGS (New Jersey Department of Environmental Protection, Trenton, New Jersey): You say that toluene is insoluble, and yet it is soluble to a certain extent. What is the concentration of toluene in the effluent?

DR. MARNELL: As it stands now, I do not know what the concentration was. I know it has not been a problem in the State of Virginia. If it did become a problem, then we would introduce either a distillation step or steaming out step to take care of any residual.

You are absolutely correct; it is not 100% insoluble. If there were trace amounts that could become objectionable, we could handle it with a simple steaming process. I do not have the exact figure.

MR. BEGGS: Thank you.

MS. EMILY A WEBBER (Oxy-Catalyst, West Chester, Pennsylvania): Are those capital costs in 1970 dollars?

DR. MARNELL: No, 1975.

MS. JACQUELINE M. FETSKO: I think you ought to mention that your border plant in Germany for many years ran medical examinations on the staff and workers that were exposed to toluene. And they found no cumulative effects after 20 years.

DR. MARNELL: Thank you for mentioning it.

MR. WATKINS: Let me make one additional comment at this point. The design requirements on this plant were that at no time during normal operations could the toluol level in the pressroom exceed 200 ppm. It is checked regularly and is operating under 100 ppm.

24 September 1975

Session III: (con.)

IMPACT OF WASTE RECOVERY AND RECYCLING ON THE ENVIRONMENT

Robert L. King
Chairman

AN ECONOMIC APPROACH TO TREATMENT OF LIQUID WASTES IN ROTOGRAVURE CYLINDER PREPARATION

Donald P. Manning*

Abstract

In the preparation and maintenance of rotogravure cylinders, printing plants are concerned about the need to comply with ever-tightening environmental standards. Long-term solutions to the problems of liquid waste handling are being sought. As State and Federal agencies more vigorously enforce regulations on discharge of heavy metals and other toxic materials, innovations in techniques must be forthcoming. This paper discusses the extent of a conceptual system required to suit, economically, the sundry problems peculiar to a given plant operation.

INTRODUCTION

Rotogravure printing requires a cylindrical printing plate where an image is etched into the surface of the plating. After being rotated in an ink bath to fill all etched depressions and after excess ink is wiped away by a doctor blade, the ink left in the depressions is absorbed by the paper, thus producing a high-quality reproduction of color work.

The preparation of the cylindrical plate for this highly sophisticated printing method requires many steps. Liquid wastes are associated with several of these steps--copper plating, chrome plating, and image etching.

The aim of this paper is to suggest options available today for the handling of these liquid wastes, with a special emphasis on economy. What is required for a given plant depends on a number of variables typical of that plant's operation. For an environmental specialist who has understood his plant's operation, the extent of a conceptual system needed to solve waste problems can be discerned.

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*Manager, Plant and Process Engineering Department, Wiley & Wilson, Inc., Lynchburg, Virginia.

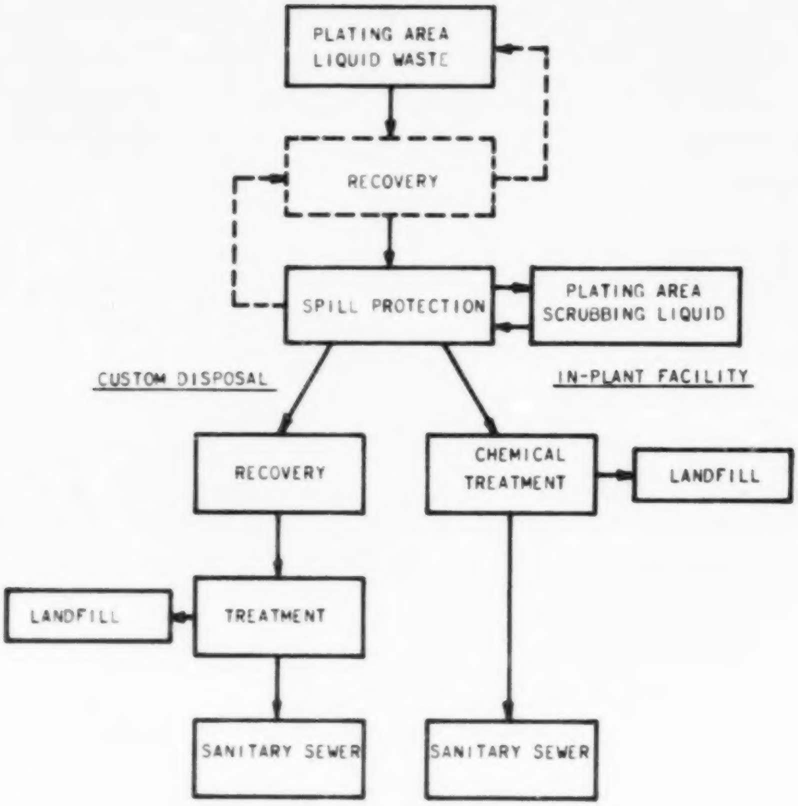

PLATING AREA LIQUID WASTE
RECOVERY
SPILL PROTECTION
PLATING AREA SCRUBBING LIQUID
CUSTOM DISPOSAL
IN-PLANT FACILITY
RECOVERY
CHEMICAL TREATMENT
LANDFILL
LANDFILL
TREATMENT
SANITARY SEWER
SANITARY SEWER

Figure 1. Liquid waste handling concept.

LIQUID WASTE HANDLING

A proposed concept of liquid waste handling would follow a step-by-step course suited economically to the pollution abatement required to meet existing State and Federal regulations. This concept, illustrated in figure 1, shows the flow of liquid waste from the copper plating, chrome plating, or image etching processes. The liquid waste is either totally or partially recovered for recycling or, in the event of spillage or dumping, passes on to a holding tank where it can be pumped to a custom disposal truck or to a chemical treatment facility before disposal to a sanitary sewer. Even though wastes from the separate processes of copper plating, chrome plating, and image etching cannot be mixed, it is possible to join the three separate treatment processes in a multiple batch series, in order to utilize the same treatment facility. The separation of the three different categories of wastes is necessary since intermixing would be hazardous and would make recovery/treatment expensive.

PLATING CHEMICALS RECOVERY

Significant cost savings can be realized in the recovery of plating chemicals, especially chrome. As other packaged units become economically feasible, recovery of other chemicals may be justified. Savings have been proved to result from recovery in the following ways (ref. 1):

1. The purchase of plating chemicals is reduced by 50 percent.
2. The purchase of chemicals to neutralize or destroy unrecovered chrome is no longer required.
3. Less water and less sewage require treatment.
4. There is no sludge to haul to landfills.

For large printing plants consuming at least 10,000 lb/yr of chrome-plating chemicals, a recovery system could be justified fully. In a cylinder-plating operation, the fume scrubber liquid will be a more valuable recoverable source than the plating tank "drag out." A recently marketed evaporator unit which costs in the range of $20,000 could be employed effectively on the scrubber liquid, if it is recirculated and allowed to become as concentrated as 2 to 3 oz/gal (ref. 2).

SPILL PROTECTION

Spills and dumped plating bath solution are not readily recovered, and thus there is need of additional provisions such as a holding tank. Spillage can result from overflowing tanks, leaks, and careless handling of chemicals. Overflowing tanks are avoided by the installation of either level alarms or predetermined flow counters. Leaks can occur in steam heating coils in plating tanks, resulting in the plating chemicals being siphoned out due to the vacuum created by condensing steam. Through the use of a conductivity meter, contaminated condensate can be detected and then diverted into a holding tank. From the plating operation, all waste liquid is collected in a holding tank, as shown in figure 2. Waste liquid from this holding tank is circulated through the scrubber, which condenses fumes from the hot plating baths, thereby limiting the amount of waste and conserving the use of plant water for the scrubbing liquid.

The options available to handle the contents of the spill-protection holding tank are several:

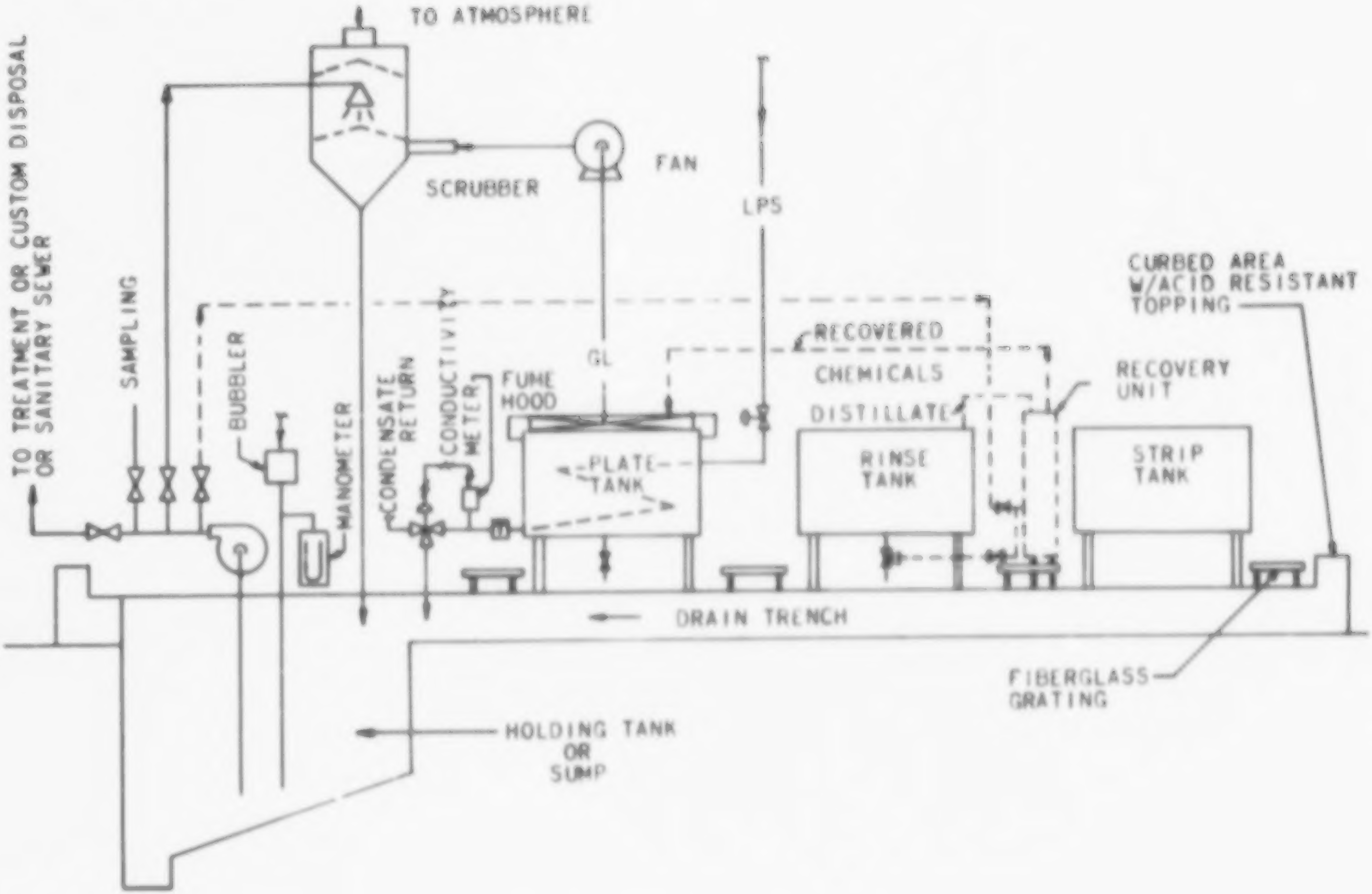
1. Plating chemicals may be recovered and recycled to the plating tank.
2. The contents of the tank can be analyzed and discharged to the sanitary sewer, if within ppm limits and pH tolerance.
3. The contents can be picked up and trucked to a custom disposal plant.
4. The contents can be chemically treated before discharge to the sanitary sewer.

In one specific plant with existing plating operations, it was found that an interim solution to disposal problems consisted of separate holding tanks, one for each category of waste (ref. 3).

CUSTOM DISPOSAL

Since recovery may not be economically justified for some of the cylinder preparation waste liquids, and since spills and dumped plating baths usually are destroyed, printing plants need provisions to handle these remaining liquid wastes. One method to accomplish the necessary disposal is to provide adequate holding tank capacity for pickup by a custom disposal tank truck. In an engineering study to compare the merits of custom disposal versus in-plant treatment, it was shown that the cost of trucking and custom disposal was half that of the cost of owning and operating a small in-plant treatment facility. This study was made in a plant that chrome plated 5 to 10 cylinders per month (ref. 4).

Since the only usual requirement of custom disposal service companies is that the waste liquid be basic rather than acidic, the stored waste liquid may be adjusted to a relatively high pH by adding caustic soda.


TO ATMOSPHERE
TO TREATMENT OR CUSTOM DISPOSAL OR SANITARY SEWER
SAMPLING
BUBBLER
MANOMETER
CONDENSATE RETURN
CONDUCTIVITY METER
SCRUBBER
FAN
GL
LPS
FUME HOOD
PLATE TANK
RECOVERED CHEMICALS
DISTILLATE
RINSE TANK
RECOVERY UNIT
STRIP TANK
CURBED AREA W/ACID RESISTANT TOPPING
DRAIN TRENCH
FIBERGLASS GRATING
HOLDING TANK OR SUMP

NOTE: Recovery system is shown in dotted lines.

Figure 2. Spill protection.

IN-PLANT CHEMICAL TREATMENT FACILITY

Good economics require that in-plant chemical treatment equipment be functional for all three categories of wastes--copper plating, chrome plating, and image etching.

One economic approach was developed whereby the three different waste liquids are handled consecutively by multiple series of batch operations. The operations below are shown in figure 3 (ref. 5):

1. The treatment of chrome plating waste in treatment tank A is the first-step reaction obtained by initially adding sulfuric or hydrochloric acid and then adding sulfur dioxide gas. This first step insures the reduction of hexavalent chromium, which is highly toxic, to the trivalent or chromic state.
2. The treatment of trivalent chrome is the second-step reaction and occurs in treatment tank B or C, where lime slurry or caustic soda solution is added to precipitate chromic salts.
3. The separate treatment of copper plating waste occurs in treatment tank B or C, where lime slurry or caustic soda solution is added to precipitate copper hydroxide. (Note the system flexibility provided by a distributor box above tanks B and C).
4. The separate treatment of iron chloride etching waste also occurs in treatment tank B or C. The metallic iron is then precipitated with a lime slurry or caustic soda solution, with the result that all metallic ions are converted into hydroxides as solids.
5. Treated batches in tanks B and C are discharged one at a time to the filter press where the sludge is collected as a solid for disposal and where the effluent is passed through to treatment tank E.
6. In treatment tank E, the effluent is treated by adding sulfuric acid to adjust the pH to the required level before releasing it to the sanitary sewer.

The design criteria for the in-plant treatment facility described above were based on a maximum production rate of 10 cylinders in an 8-hour operating shift.

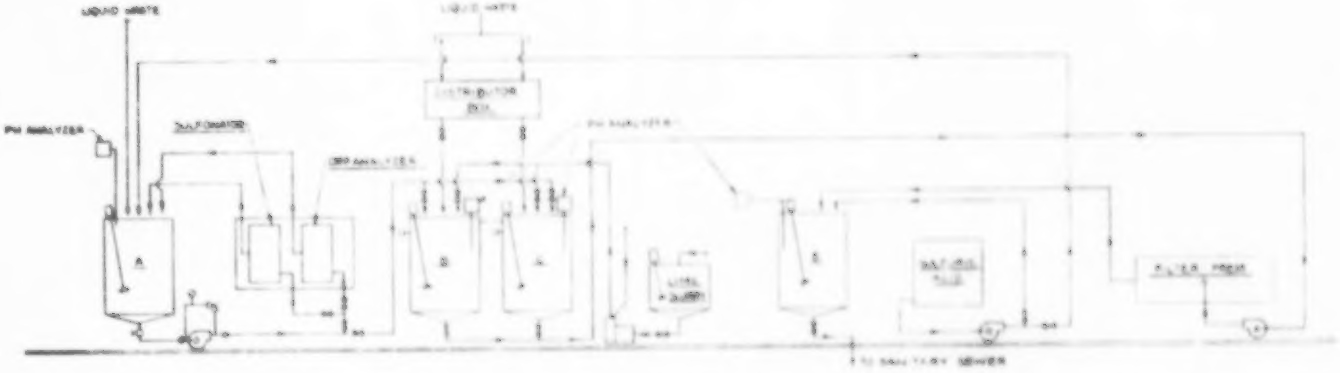

PH ANALYZER
LIQUID WASTE
SULFONATOR
ORP ANALYZER
LIQUID WASTE
DISTRIBUTOR BOX
PH ANALYZER
A
B
A
LIME SLURRY
E
FILTER PRESS
TO SANITARY SEWER

Figure 3. In-plant treatment scheme.

SUMMARY

Many printing plants using the rotogravure method have already mounted continuing environmental programs. These programs include consideration for: 1) the recovery of chemicals from rinse water, 2) improved practices for handling chemicals, 3) spill protection, 4) fume scrubbing, 5) segregation of the various categories of liquid wastes, 6) water conservation, and 7) custom disposal or in-plant treatment.

Careful scrutiny of the needs of one's own operation is the all-important first step in attaining long-range solutions to problems of waste handling. Customer engineering is required to solve individual problems that each printing plant presents. Through innovations on the part of the designer toward the greatest practical use of the facilities required, the safe disposal of liquid wastes in rotogravure cylinder preparation can be economically handled.

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2. Telephone Communication with Mr. R. G. Jump, Manager, Distributor Sales, Chemical Recovery Systems, at Corning Glass Works, Corning, New York, August 8, 1975.
3. Clarence T. Sloan, Jr., "How to Handle Spent Plating Solutions," Industrial Waste, November-December 1974.
4. Unpublished engineering report, J. L. Montague, chemical engineer, Wiley & Wilson, Inc., June 1975.
5. Unpublished engineering report, R. E. Lipscomb, design engineer, and R. W. Nash, retired chemical engineer, Wiley & Wilson, Inc., December 1970.

DISCUSSION

MR. W. N. FINGLAND (International Paper Company, Clinton, Iowa): Are there any problems with the disposal of the resulting solids?

Second question: A filter press is pretty darned expensive for a medium-sized operation. Have you seen, or do you know now of the use of centrifuges?

MR. MANNING: Yes. To answer the first question, with a filter aid, the filter press does a very good job. If there is any carry-over, and you are allowed to dump into the municipal sewer, dumping will handle that satisfactorily.

The cost of the particular type filter press that was used was in the neighborhood of $30,000.00 to $40,000.00, I believe. It is a leaf-type filter press. I might say here that the total cost for this in-plant treatment facility was about $130,000.00. So that was a major cost item in the design of this facility. Does that answer your question?

MR. FINGLAND: Except as to the disposal of the sludge.

MR. MANNING: The sludge is handled by putting it into Dempster-Dumpsters and hauling it away to landfills.

MR. FINGLAND: No problem with that?

MR. MANNING: No real problem. Any other questions?

MR. ALVIN SALTZMAN (New Jersey Bureau of Solid Waste Management, Trenton, New Jersey): I have a response to that statement. Actually, we are having problems with landfills, particularly with leachate. I can anticipate that in the future, if not now, at least in New Jersey landfills, you will have some problems with disposal of the materials containing heavy metals that were shown coming from the precipitators.

RECOVERY AND REUSE OF ORGANIC INK SOLVENTS

R. L. Harvin, Ph.D.*

Abstract

Environmental and OSHA requirements are coupled with solvent supply and economic factors to make examination of solvent recovery and reuse important for the solvent-using industries. Solvent recovery process choices are discussed. For most solvent drying applications, with relatively low concentrations in the solvent-laden air, activated carbon adsorption is shown to be most suitable. Some theory and details of the adsorption process are presented. Applications of the carbon adsorption and solvent separation processes are discussed for several cases involving either single solvents or mixtures of solvents. A case history is presented of a gravure plant solvent recovery system that has been in operation since 1971. The recovery system treats all the plant exhaust and recovers 38,500 gal/wk, of which 12,900 gal/wk are exported for reuse in ink manufacture and the balance is reused for ink dilution. The overall efficiency of the solvent recovery and recycle system is about 90 percent. The consumption of solvent has been reduced from 2,215,000 gal/yr to about 215,000 gal/yr. The solvent cost savings and the independence from solvent supply problems are cited as valuable justifications for this system.

INTRODUCTION

This paper was prepared for a conference focusing on the environmental aspects of chemical use in printing operations. Thus, in the context of this conference, solvents are those used in inks as a medium to carry pigment to the surface of a web. However, in the broader sense, we are discussing any process wherein organic solvents are used in the application of a dissolved material to a moving web or film. The major examples of such processes and the ones to be referred to in this paper are: (a) gravure or similar printing, and (b) continuous coating on paper, metal, or plastic films. In addition, many other processes could be mentioned, all of which have the same essential elements: namely, a) application of a high-solvent-content material to the surface of a moving web or film; b) rapid evaporation of solvent to enable further processing or handling; c) evaporation accomplished by movement of heated air across wet surface; and d) solvent-laden air exhausted from system.

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*Engineering Specialist, C&I/Girdler Inc., Louisville, Kentucky.

On examination of modern industry, one finds the concept of recovery and reuse of chemicals and solvents is not a uniformly accepted practice. Certain highly sophisticated industries have always recovered every BTU or pound of material and have indeed gained an edge in the competitive race by a fractional improvement in such schemes. Other industries have been quite content to use materials on a once-through basis and have concentrated their competitive efforts in other areas. The uniformity that is found is that, within a particular industry, all members treat the concept similarly. One must conclude that through experience and with mutual assurance, each industry has moved in the direction of maximum profits. In a perfectly free society, abundant in raw materials and energy, this is the conclusion that economic theoreticians would predict. However, we are no longer in a free society, abundant in raw materials and energy. Out of necessity, we are giving up the free society in favor of limitations that are intended to preserve our resources, restore the environment, and improve the quality of life. Industry now has the problem of reexamining its previous conclusions in light of these new restraints.

Emission Restraints

The most compelling of the new factors influencing consideration of solvent recovery are the emission control regulations that are now in effect in most States. Although there are differences in these regulations, it is safe to predict that the ultimate effect will be that users of solvents will gradually reduce emissions to the environment from 100 percent of the solvents used in their processes to the 2- to 10-percent range.

OSHA Restraints

Under the influence of the OSHA health and safety regulations, the management of solvent-using plants will have to give increased attention to lowering the concentration of solvent vapors within their plants. The preferred way is by improved plant design to prevent escape of the solvents from the process equipment. Solvent vapors that connot be contained must be recaptured by exhausting the solvent-laden air from the area and this adds to the plant emission problem.

Solvent Supply Restraints

The current shortage of supply of all types of solvents is an accepted fact and the long-term trend is certain to be of increased scarcity. Conditions exist which can cause a tenuous situation to develop into an absolute disappearance from the market of certain raw materials. The quantities of solvents used by many industries are such that it is impractical to inventory more than a few days or weeks supply. For example, it is not uncommon for a gravure printer to consume 20,000 to 40,000 gallons of solvent per week and to depend on deliveries every few days. With application of the solvent recovery and reuse principles available today, it is possible to eliminate such dependence and remove the spector of plant shutdown due to a solvent shortage.

Economic Restraints

The cost of solvents has increased dramatically and the occurance of spot shortages can cost additional premiums in order to maintain plant operations. Such economic pressures emphasize the importance of examining solvent recovery and reuse. However, due to the increased cost of facilities and their operation, solvent recovery projects do not always show an attractive return on investment. If it were so, then everyone would probably be doing it--for the reason cited earlier. When considered as a resolution to a problem involving the other factors mentioned above, solvent recovery and reuse may be easily justified.

PROCESS CHOICES

Industry has available a number of alternate commercial processes for handling solvent emission control and occupational health and safety problems. First, consideration should be given to improvements to the design of the basic equipment for utilizing the solvent efficiently and keeping it physically contained within the system. Then through the use of incineration, adsorption, absorption, or condensation, the emissions to the atmosphere can be controlled. When the objectives also include solvent recovery and reuse, only adsorption with activated carbon has much application. Under certain conditions, condensation and/or absorption could be used in conjunction with one of the other processes to achieve both solvent recovery and the desired degree of emission control.

The outstanding advantage that the activated carbon adsorption process has over other solvent recovery processes is its ability to remove all the organics (solvents) from the air regardless of variations in concentration and humidity conditions. Concentrations of 3,000 ppm and below can be recovered at high efficiency leaving only a few ppm in the effluent airstream. With due allowance for explosive mixtures, concentrations above 3,000 ppm can be handled at even higher efficiency.

The condensation process, by comparison, can recover only those constituents above the saturation concentration at the condensing temperature. Even with refrigeration, condensation as a means to recover most commercial solvents would only be practical at vapor concentrations well above 10,000 to 20,000 ppm. Then after condensing, the residual solvent concentration would be several thousand ppm and probably well above emission requirements. The usual 25- to 50-percent LEL safety requirement for solvent-laden air systems therefore precludes the use of condensation for solvent recovery in the usual printing and coating operations. In the petroleum and petrochemical industries, where condensation has application, the residual gas stream would either be recycled to the process to pick up more solvent or would be treated by another control scheme before release to the atmosphere. Closed-loop systems may be operated safely using an inert carrier gas, such as nitrogen, or using air if the solvent is nonexplosive, such as methylene chloride.

The absorption process depends on a component's solubility in a relatively nonvolatile absorbent liquid. Solubility is directly related to vapor concentration, so absorption at low vapor concentration is highly inefficient. For solvent recovery applications with concentrations in the 0- to 3,000-ppm range, the absorption process requires excessively large equipment. Thus, the process is not suitable for solvent recovery for the printing and coating operations. There are special applications for a direct contact absorber or scrubber on a solvent-laden air stream as a pretreatment before going to another emission control scheme.

ADSORPTION PROCESS

The adsorption process is dependent on the property of a solid surface to capture and accumulate molecules of a fluid with which it comes in contact. All molecules, whether gas, liquids, or solids, are subject to this phenomenon but the degree to which each material is affected is a characteristic of that material. By this process, constituents of an airstream may be selectively adsorbed or removed by materials known as adsorbents.

The exact mechanism by which adsorption takes place is still uncertain. Most theories attribute the phenomenon to the forces causing cohesion in solids and liquids. These forces can be divided into two groups: intermolecular or van der Waals forces causing physical adsorption, and chemical forces causing chemisorption. In the former, the adsorbed molecules are preserved intact while in the latter the adsorbed molecules break up into atoms or radicals which are bound separately to the surface as in chemical combination. In physical adsorption the surface of the adsorbent may be covered with multiple layers of molecules depending on the intermolecular forces. In chemisorption the mechanism is limited to a monolayer.

Most applications of the adsorption process to recovery of organic vapors involve only the physical adsorption mechanism. The process strongly resembles condensation and is accompanied by the liberation of heat of the same order of magnitude as the heat of liquifaction. The process can be reversed by supplying heat of this magnitude, whereby the adsorbent surface is regenerated.

It is apparent that the effectiveness of a solid to adsorb molecules is strongly related to the amount of interfacial surface. Therefore, to achieve a high degree of adsorption, it is expedient to create the maximum obtainable surface area within the solid phase. Commercial adsorbents, such as activated alumina, silica gel, and activated carbon, contain a large number of micropores having hundreds or thousands of square meters of surface within a gram of solid. Adsorption process equipment is designed to contain a quantity of adsorbent in small pellet or granular form, suitably arranged so that the adsorbate-containing air can flow through the entire quantity. The dimensions of the bed of adsorbent and the flow of air are selected so that adsorption can be substantially complete in the time of contact. After some period of flow, the adsorbent will become saturated with the adsorbate and will cease to function. When this occurs, the adsorbent must be replaced or regenerated.

Vapor phase adsorption is essentially an exothermic gas-solid equilibrium process, and conditions which shift the equilibrium toward saturation usually improve the process. Consequently, adsorption will take place more efficiently near the dew point and it is beneficial to operate at the lowest practical temperature. Regeneration of the adsorbent can be accomplished by raising the temperature of the system and supplying sufficient heat to break the adsorption bonds. However, some molecules are more difficult to remove from the microporic structure then others and tend to remain as a residual or "heel."

If the vapors to be adsorbed consist of several components, the adsorption of the various components will not be uniform. Generally, these components are adsorbed in an approximate inverse relationship to their volatilities. Hence, when air containing a mixture of organic vapors is passed through a bed of adsorbent, the vapors are equally adsorbed at the start; but as the amount of higher boiling constituent retained in the bed increases, the more volatile component revaporizes and moves on through the bed to a more favorable adsorption site. Eventually some of the more volatile constituent will be forced out completely and can be detected in the effluent. The higher boiling component has thus displaced the lower boiler component, and this mechanism if continued would result in only the highest boiling component being retained on the adsorbent.

SOLVENT RECOVERY DESIGN

The detailed procedures for the design of activated carbon adsorption processes are well documented in the literature. These lead to the selection of such items as carbon bed dimensions, number of adsorber vessels, cycle timing, regeneration conditions, precooling requirements, and condensing duty. This paper will not consider these design principles but will discuss questions of application to the overall solvent recovery problem.

Basic Process Flow Diagram

In the typical solvent recovery application, illustrated in figure 1, activated carbon is used as the adsorbent, and multiple vessels (adsorbers) containing the carbon are provided so that one can be off-line for regeneration while the other(s) are actively treating the solvent-laden airstream. Adsorbers may vary considerably in design and in orientation of the carbon bed. However, with the usual design criteria, carbon beds are 16 to 24 inches thick and composed of pelleted or granular material in the 1/16- to 1/4-inch size range. Pretreatment of the solvent-laden airstream frequently consists of dust removal and cooling. For regeneration, steam is used in the reverse direction through the carbon bed to clean the outlet portion most thoroughly. The steam and solvent vapors are condensed and either decanted for reuse or further processed by distillation or other means.

The process, as illustrated, represents a sizeable number of actual installations. The plants are simple, they work well, and the carbon gives years of active service. However, conditions may exist which require special attention.

Nonregenerable Constituents

Process generated particulates, airborne plant dust, and low-vapor-pressure components from the ink, coating, or web may be present in minute quantities but can accumulate on the carbon bed to substantial amounts after a period of operation, since they are not removed from the carbon during regeneration. Also, certain constituents from the ink or coating

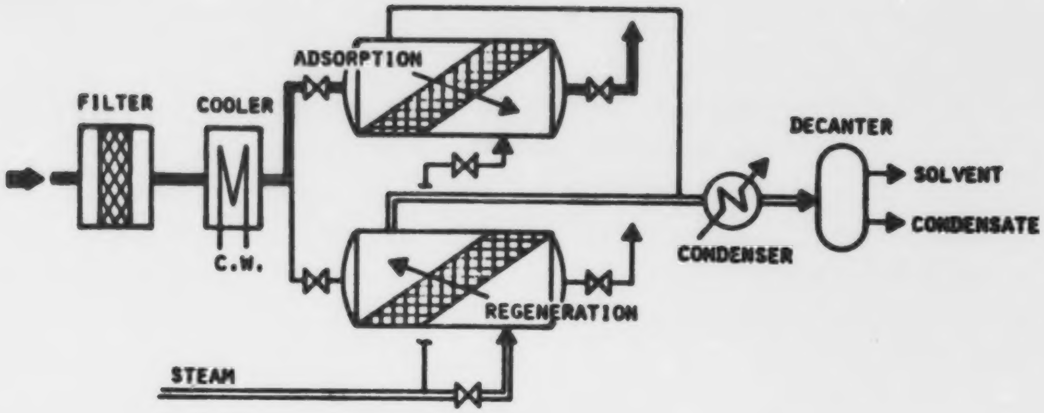

Figure 1. Adsorption process flow diagram.

may have a tendency to polymerize after adsorption or during regeneration under the influence of the heat and possible catalytic effect of the carbon or impurities.

The dependence of the process on available surface and on freedom of molecular movement in the adsorbent pore structure make it evident that any physical blockage will destroy the ability of the adsorbent to perform. High-efficiency particulate filters should be provided unless the cleanliness of the airstream is assured by other means. Nonregenerable vapor components can usually be removed from the airstream by providing a carbon bed filter or sacrificial bed. Initially this bed will adsorb to saturation all components of the vapor. Gradually, the lower boiling material will displace all other components and the sacrificial bed will be replaced. Prevention of polymerization products on the carbon requires a knowledge of the chemistry involved in order to predict how to avoid such damage.

Variation of Solvent Composition

Prolonged use of the carbon on solvent-laden air of a particular solvent composition results in the formation of a heel composed of each molecular species in "equilibrium" with the vapor composition. If the inlet airstream composition is altered in any way, the carbon will shift toward a new heel composition and the recovered solvent composition will show the effects of this shift until a new heel composition has been established. If air containing a new species of solvent is passed through the adsorber, the new species will compete for adsorption sites with those forming the heel from previous use and the recovered solvent will be contaminated by each species of solvent on the carbon. Such contamination may persist through several cycles.

SOLVENT REUSE FLOW DIAGRAMS

Single Solvent

If a single solvent (1 species) is used, its recovery for reuse can be very simple, as illustrated in figure 2. The solvent vapor and regeneration steam will be condensed. If two phases are formed, separation is effected and frequently the solvent can be reused without further treatment. In case of partial or complete solubility in water, distillation may be required to produce a reusable solvent as well as a reusable or disposable condensate. Dehydration schemes for many solvents are described in the literature.

Mixed Solvent

If a solvent composed of two or more species is used, then the air from the drier will contain a mixture of the solvents and these will be adsorbed and recovered together, as illustrated in figure 3. If, upon condensation, two phases are formed, separation by decantation may produce a mixture suitable for reuse. However, due to variations of volatilities in the drier, variations of recovery efficiency in the adsorption, and variation of solubility in water, the recovered solvent mixture will differ slightly from the original composition. Based on a laboratory analysis, the composition can be restored by "doctoring", using fresh solvents.

If the solvents are partially or completely soluble in water, then the condensed mixture must be distilled to dehydrate. In so doing, the organic material will be separated into several fractions which, upon

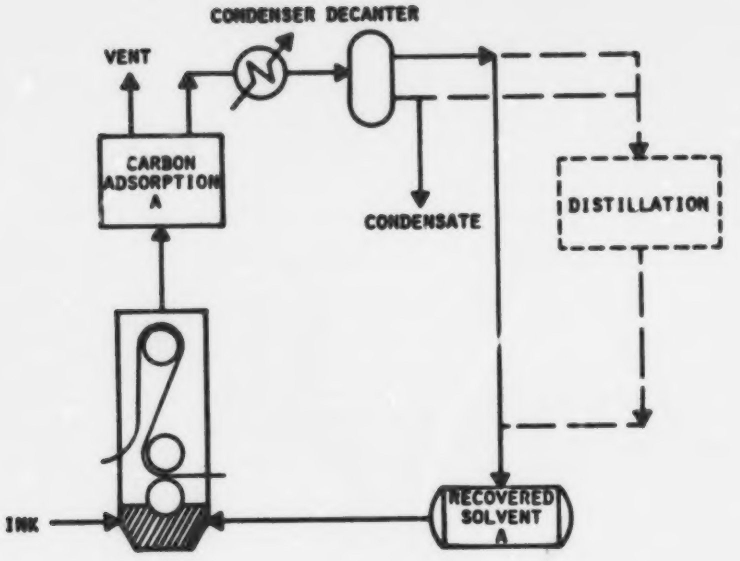
CONDENSER DECANTER
VENT
CARBON ADSORPTION A
CONDENSATE
DISTILLATION
INK
RECOVERED SOLVENT A

Figure 2. Solvent reuse diagram--single solvent.

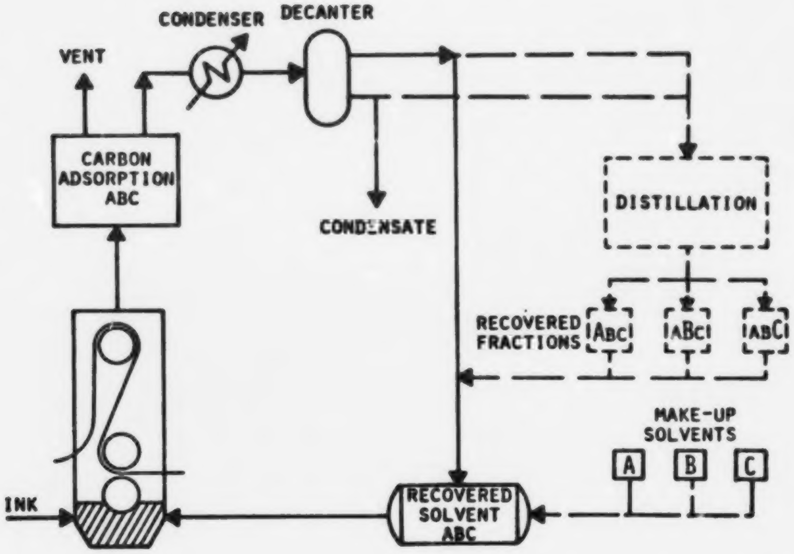
CONDENSER
DECANTER
VENT
CARBON ADSORPTION ABC
CONDENSATE
DISTILLATION
RECOVERED FRACTIONS
ABC
ABC
ABC
MAKE-UP SOLVENTS
A
B
C
INK
RECOVERED SOLVENT ABC

Figure 3. Solvent reuse diagram--mixed solvents.

analysis, can be recombined to yield the desired solvent formulation.

The distillation need not be designed to produce solvent fractions of the same composition or degree of purity as the commercial solvents used to prepare the original formulation. Solvent mixtures, whose components coexist simply as the result of mixing dissolved pigments, resins, driers, and vehicles to prepare an ink or coating, are unique mixtures and may pose difficult problems of separation. The components are seldom members of a single family or homologous series of solvents and they range over the extremes of polarity. Such systems invariably contain potential constant-boiling mixtures or azeotropes. Liquid-liquid extraction and azeotropic and extractive distillation can be used to circumvent the formation of some constant-boiling mixtures. However, as an alternative to the expense of such a complex separation system, careful consideration should be given to reformulation of the ink or coating to allow the use of solvent fractions only partially separated or of azeotropic composition.

Success or failure of a recovery and reuse effort can hinge on a company's willingness to face this problem. The marketing organization insists that a product of a certain quality and uniformity be produced; the product development group insists that the formulation used in their product development program be adhered to; the production group wants to produce the desired product efficiently; the environmental group interprets the regulations and specifies the ambient and effluent requirements; and the facilities group, which has the responsibility for providing a solvent recovery plant to please everyone, must do so within a budget and schedule.

Multistage With Different Solvents

If the solvents used in successive stages of printing or coating differ, either in percentage composition or species, then the air from the driers will contain a blend of all solvents and these will be adsorbed and recovered together, as illustrated in figure 4. The condensed solvent mixture, whether soluble in water or not, will have to be separated into fractions by distillation in order to reuse in the separate stages. If the formulations for the stages differ only in percentage composition, then the components need not be highly segregated in the distilled fractions. On the other hand, if the formulations differ in the components,

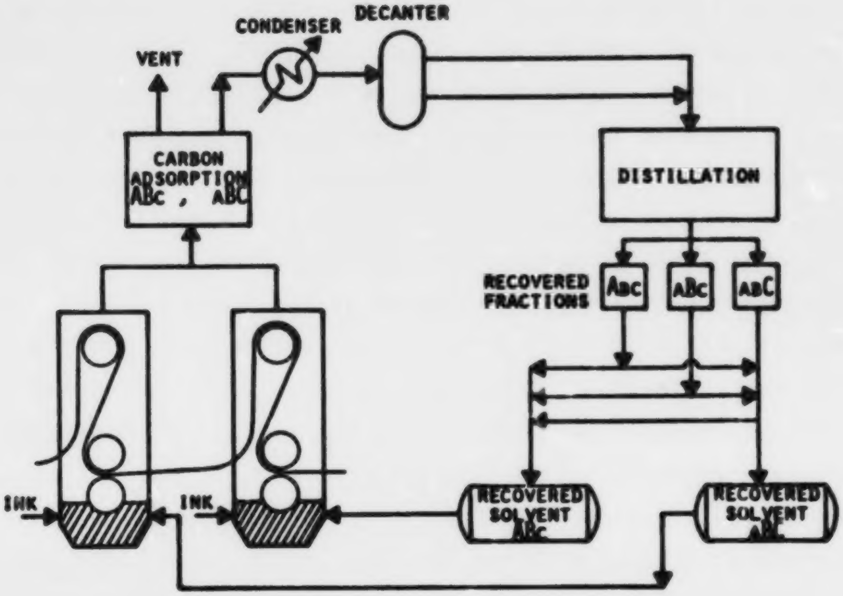
CONDENSER
DECANTER
VENT
CARBON ADSORPTION ABc , ABC
DISTILLATION
RECOVERED FRACTIONS
Abc
ABc
AbC
INK
INK
RECOVERED SOLVENT ABc
RECOVERED SOLVENT

Figure 4. Solvent reuse diagram--multistage with different solvents.

a much higher degree of segregation may be necessary in the distilled fractions. This raises questions of compatability of the ink or coating with solvents which are normally not used in the formulation. Here again, cooperation of the various interests within a company is needed to establish realistic design requirements.

In the extreme, if complete segregation of the solvents is necessary, it may be preferred to prevent the initial mixing in the drying airstream, by completely evaporating the solvent from one stage before going into the next stage. Separate adsorption and recovery systems would be needed for the different solvent-laden airstreams. This could result in an intermittant-continuous process which is practical in the case of certain processes but highly impractical in a high-speed multipress gravure-type operation.

Separate Products with Solvents of Different Percentage Composition

If solvent formulation, differing only in percentage of components, are used in separate products run either simultaneously on parallel presses or intermittantly on a single press, the air from the driers may be handled by a single adsorption system if distillation is required for separation. This is illustrated in figure 5. In this scheme, the composition being recovered at any time is effected by the heel of solvent from previous operation and thus does not exactly correspond to the composition of solvent being used in the product. Alternately, if the solvents are insoluble in water, separate adsorption systems with decantation for each formulation may be practical.

Separate Products with Solvents of Different Components

If solvents containing different species are used in separate products, run either simultaneously on parallel presses or intermittantly on a single press, the air from the driers should be handled by separate adsorption systems for each formulation, as shown in figure 6. The separate condensed phases would be either decanted or distilled as required. However, any distillation system needed would probably be less complex due to the complete isolation of the different chemical species.

A CASE HISTORY

The Standard Gravure Corporation of Louisville, Kentucky, installed solvent recovery facilities in 1971. At the time, public awareness of the environment was in full bloom. Some communities had established emission regulations while others, including Louisville, were just beginning to analyze the problem. Only "pessimists" were forecasting an energy shortage and the price of solvents had been relatively stable at 18 to 20 cents per gallon. Nevertheless, for reasons of good community relations, the Standard Gravure management made a decision that airborne solvent emissions were to be controlled and that recovery and reuse of the solvent were prime objectives.

Standard Gravure has its plant facilities in a complex of multistory buildings also housing the corporate offices and publishing facilities of the jointly owned Courier Journal and Louisville Times newspapers. The entire complex is air conditioned from a central utility area. The air exhausted from the ovens and other operating units in the printing areas

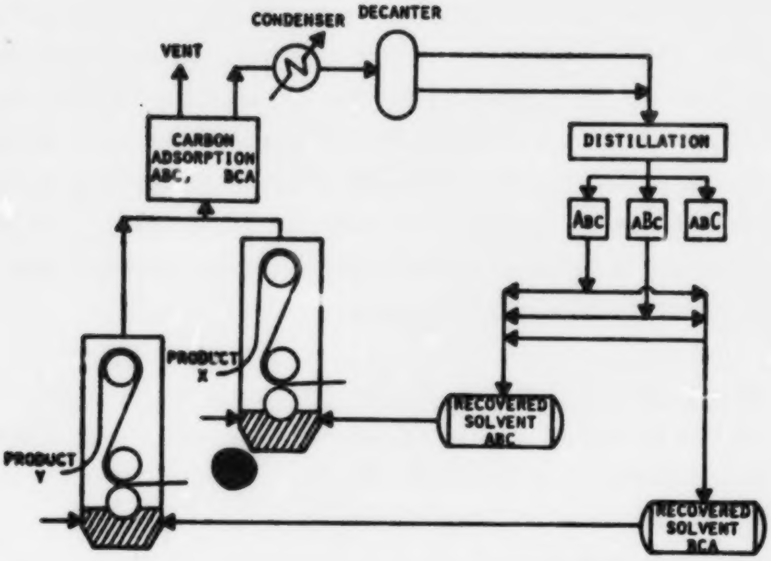
CONDENSER
DECANTER
VENT
CARBON ADSORPTION ABC, BCA
DISTILLATION
Abc
aBc
abC
PRODUCT X
PRODUCT Y
RECOVERED SOLVENT ABC
RECOVERED SOLVENT BCA

Figure 5. Solvent reuse diagram--multiple products with similar solvents.

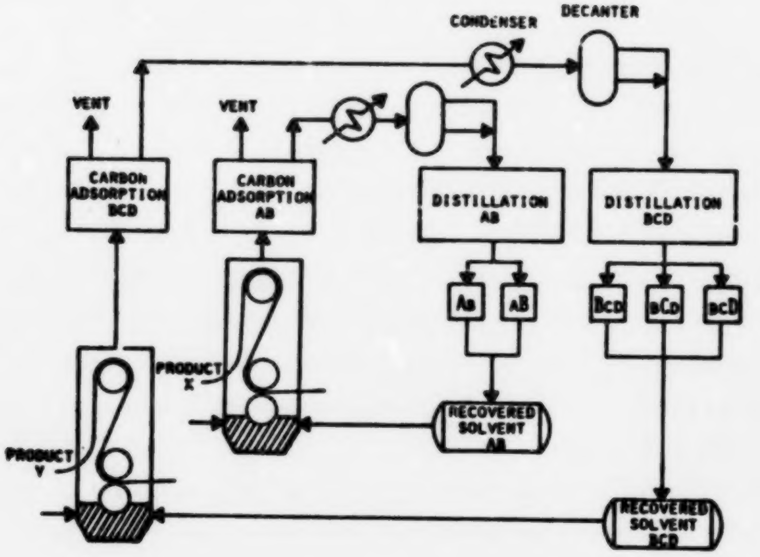
CONDENSER
DECANTER
VENT
VENT
CARBON ADSORPTION BCD
CARBON ADSORPTION AB
DISTILLATION AB
DISTILLATION BCD
Ab
aB
Bcd
bCd
bcD
PRODUCT X
PRODUCT Y
RECOVERED SOLVENT AB
RECOVERED SOLVENT BCD

Figure 6. Solvent reuse diagram--multiple products with different solvents.

is replaced by fresh, conditioned air distributed to various locations in the building complex. Solvents that escape from the presses or remain temporarily in the printed product are kept at a tolerable level by room exhausts in the printing areas. Thus, within the plant buildings, air flow is toward the printing areas and solvents are not distributed throughout.

Plant emission tests were set up to study oven and room exhaust solvent concentrations on a 24-hour basis. Inventory records of the quantity of solvent consumed indicated that the plant should be designed to recover approximately 2 MM gal/yr. On the basis of a straight average, this is a usage of 1,800 lb/hr at a concentration level of 400-500 ppm at projected exhaust volumes. However, the study of the actual concentration in the exhaust streams from individual oven discharge blowers showed variations ranging up to five times the average. The room exhausts were found to contain 100-300 lb/hr, thus indicating that they should be included in the solvent recovery system. Also, using the records of the preceding year, the actual operating times and exact quantities of solvents used were analyzed. A design basis then was selected which would handle the exhausts under all extremes of operation.

The gravure printing operations followed the time honored procedure of maintaining several bulk solvents with different drying speeds and solvency. Depending upon the job specifications, different amounts of solvents such as VM&P naphtha, toluol, xylol, etc., were used as diluents of the inks to obtain certain printing characteristics. These solvents are relatively insoluble in water so that an organic solvent phase could be separated from the regeneration steam condensate. Distillation would be required to separate the organic phase into fractions with properties similar to the solvents used. However, to avoid the expense and complexity of a separation plant, investigations proceeded into the possibility of using a single formulation of a "base solvent"[1] that would handle all but proof press operations and specialty jobs. This study had to take into account the solvent used by the ink manufacturer since it would also be recovered. With favorable indications that such could be done, a solvent recovery plant was installed based on decantation and reuse of the solvent mixture.

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[1] Patent pending on "base solvent" formulation by J. K. Anderson.

Process Description

A simplified process flow diagram is shown in figure 7. There are two gravure printing rooms, each designed for oven and room exhaust air volumes of 120,000 acfm. The exhaust plenum from each area has an automatic relief to the atmosphere in the event of an interruption in the solvent recovery plant. Solvent-laden air from each area flows through separate two-stage high-efficiency filters to remove paper and ink particles. The air to the gravure ovens is drawn from the pressroom, which is supplied with filtered air so that atmospheric dust does not represent additional load to these filters. The pressroom is held at approximately 75° F and 50 percent relative humidity and the combined oven and room exhausts range between 100° and 110° F. With these conditions, no further cooling or humidity control is required for efficient adsorption or plant safety.

From the filters the airstreams flow into two booster fans with automatic control to adjust to the capacity variations of the gravure presses.

Six activated carbon adsorbers are provided and each has inlet valves on the air ducts so that it can be switched in and out of service independently. Four adsorbers are active, each handling 25 percent of the total flow, and the two adsorbers not in service undergo a two-stage regeneration made up of back-flow steaming followed by forward-flow cooling with air. The four active adsorbers are always sequenced so that they are equally distributed on the loading cycle; that is, they are 25 percent of the loading cycle apart. When one adsorber becomes loaded to capacity with solvent and begins to break through, the others are 75, 50, and 25 percent loaded. In order to maintain this relationship, it is necessary to have balanced flow to the four adsorbers.

By automatic selection, samples of each of the purified air exhausts are withdrawn and a composite analysis of the total hydrocarbon content is continuously recorded. When a carbon bed becomes saturated with solvent, its breakthrough is detected by its effect on the composite sample.

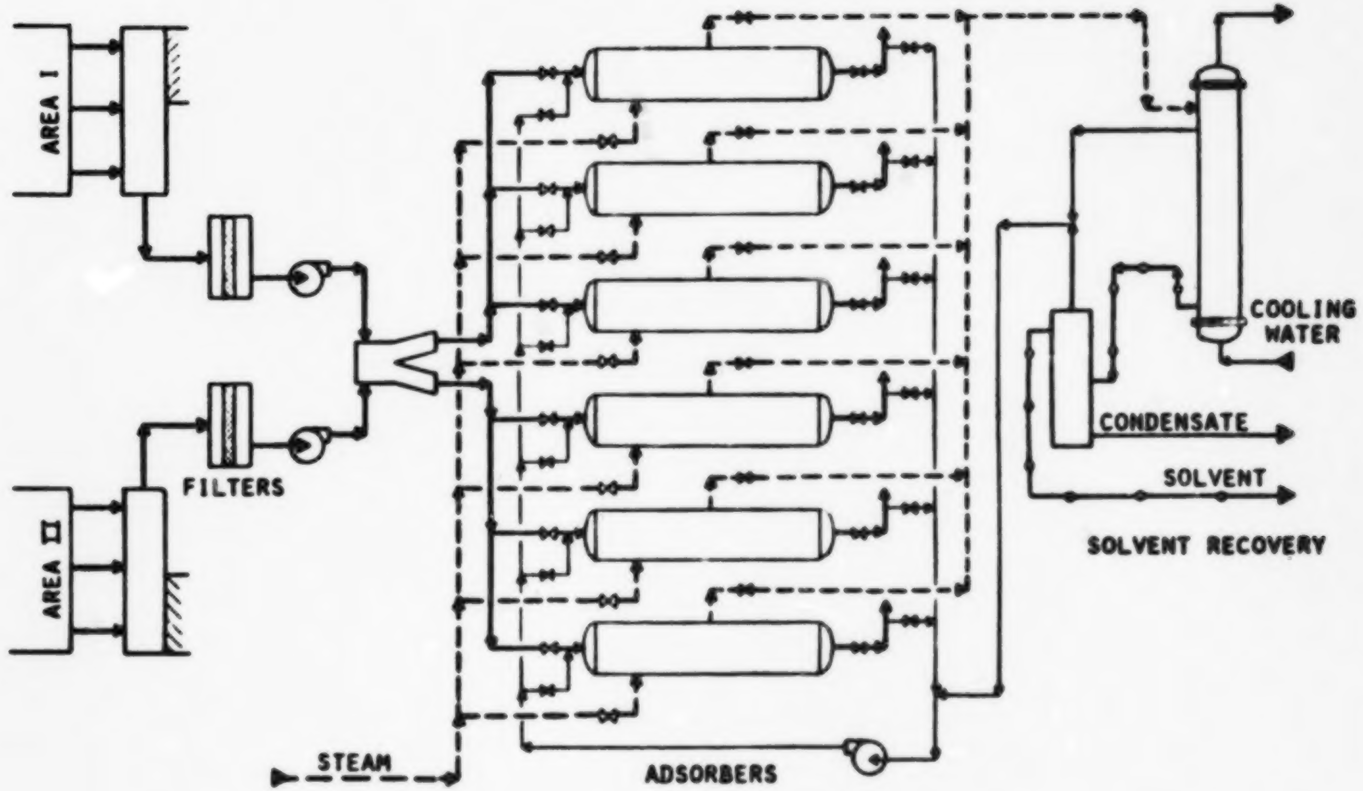
AREA I
AREA II
FILTERS
STEAM
ADSORBERS
COOLING WATER
CONDENSATE
SOLVENT
SOLVENT RECOVERY

Figure 7. Simplified process flow diagram--Standard Gravure Corp.

At this point, the air flow is diverted from the saturated adsorber to the one having been steamed and cooled.

Regeneration is accomplished by the use of low-pressure steam flowing equally through all portions of the carbon bed. The mixed steam and solvent vapors from the adsorber are condensed and the two liquid phases are separated by decantation. The solvent flows directly to the 20,000-gal-capacity underground storage system, ready for reuse. The separated solvent contains approximately 200 ppm of dissolved water and with proper decantation there should be no separation of water from the solvent as it is reused. However, the underground tankage allows additional time for minute water droplets to settle out.

The Solvent Recycle System

In this plant, all solvent-laden exhausts are treated and the entire plant is operated under conditions to minimize loss of solvents. Since the gravure ink, which is purchased outside, contains an appreciable quantity of solvent, the recovery system always generates a net surplus which must be exported from the plant. The quantity exported is approximately equal to the solvent in the purchased ink, less any losses in the system. The exported solvent is used by the ink manufacturer in formulation of new ink supplies for the gravure plant. This recycle system for the "base solvent" is illustrated in figure 8. The plant also maintains a supply of xylol for operation of proof presses and Lactol for Spectacolor work. These solvents are the only ones still purchased and they are recovered with the base solvent.

During 1973 and 1974, the average quantity of solvent recovered was 38,500 gal/wk. Of this amount, an average of 12,900 gal/wk were exported to the ink manufacturer and 25,600 gal/wk were reused for dilution and minor purposes such as washup, cylinder cleaning, etc. The use of xylol and Lactol during this period was about 1,500-2,100 gal/wk. The quantity of base solvent in inventory throughout this period averaged 12,000 gal or about a 2-day supply. In the manufacture of ink, 1,800-2,000 gal/wk of additional solvents were used. If the base solvent composition required some adjustment, appropriate additions of the needed solvent could be made by the ink manufacture.

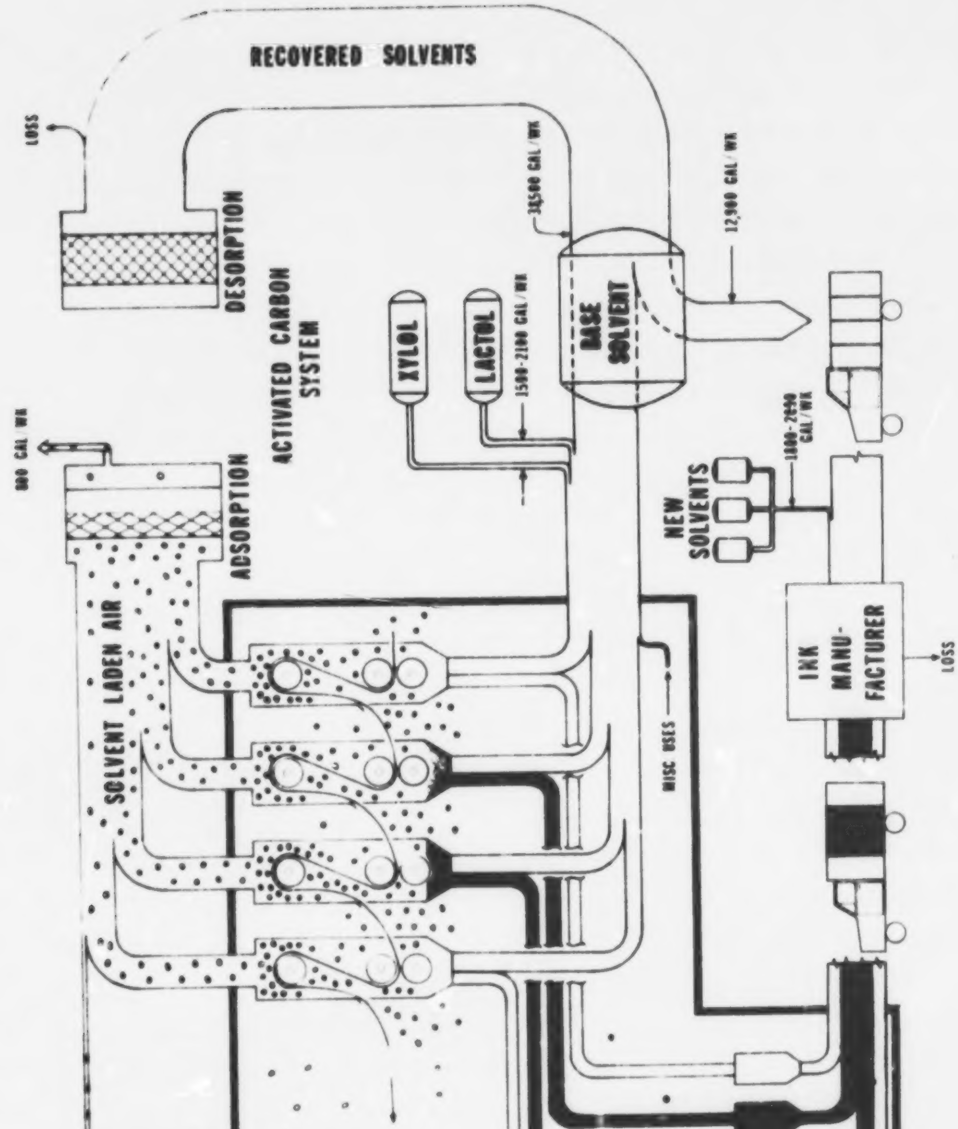
RECOVERED SOLVENTS
LOSS
DESORPTION
ACTIVATED CARBON SYSTEM
800 GAL/WK
ADSORPTION
38,500 GAL/WK
12,900 GAL/WK
XYLOL
LACTOL
1500-2100 GAL/WK
BASE SOLVENT
NEW SOLVENTS
1800-2800 GAL/WK
SOLVENT LADEN AIR
MISC USES
INK MANU-FACTURER
LOSS
PRODUCT
LOSS

Figure 8. Solvent recycle system.

The overall solvent cycle efficiency is about 90 percent based on total solvent imports of 42,600 gal/wk. This total is derived from plant records which take into account all solvents brought into the plant in the form of production ink, proof ink, and the xylol-Lactol solvents.

Of the 4,100 gal/wk apparent loss, approximately 800 gal/wk can be accounted for as leakage through the carbon adsorbers. The charts recording plant effluent concentration trace variations from a low of about 5 ppm immediately after a fresh adsorber is online, up to about 15 ppm at the end of a cycle. An approximate mean value of 8 or 9 ppm amounts to a 2-percent breakthrough loss, based on average inlet air concentrations of 400-500 ppm. Other solvent losses include; solubility in the decanter condensate, washup uses, solvent remaining in the product and handling losses.

Regular chromatographic analyses of the base solvent are run to make sure that the major components are within the established tolerable limits. Over several years of operation, compositions have stayed within these limits remarkably well. The use of xylol for proofing and Lactol for Spectacolor have offsetting effects and the additions made by the ink manufacturer have been sufficient to maintain the base solvent within specifications.

The Standard Gravure Corporation considers the solvent recovery system a great success story. Not only has the project met all of the technical objectives, but it has been given credit for keeping the plant running by making it independent of solvent supplies. Since the solvent recovery system is the major source of solvent for the ink manufacturer, the assurance of this supply is an additional benefit of equal importance. During the petroleum shortage of 1973 and the resulting energy crunch, crude oil was diverted from production of naphtha to other more profitable petrochemicals. Suddenly, naphtha was in short supply and its price soared to 56 cents per gallon, with some offered for as high as 80 cents per gallon. This was not a serious problem for Standard Gravure and its ink manufacturer, since it had reduced its solvent consumption form 2,215,000 gal/yr to 215,000 gal/yr.

The price of solvents has fluctuated considerably and is currently about 36 cents per gallon. It is obvious that the rate of return on investment has improved considerably as compared with 1971.

ACKNOWLEDGMENTS

The author wishes to acknowledge the gracious consent on the part of Standard Gravure Corporation in allowing publication of information concerning its plant and operations. Also acknowledged is Mr. Jack Uhl, Production Engineer, whose helpful cooperation during the preparation of this paper was greatly appreciated.

DISCUSSION

MR. ALVIN R. SALTZMAN (New Jersey Bureau of Solid Waste Management, Trenton, New Jersey): It is a very interesting paper. And I think it really gets down to the nitty-gritty of some of our recycling problems.

You have shown a closed loop system having variable inputs, composition, and other factors. For this type of system, feeding back directly into the printing system, the matter of stability and control becomes a very important factor. Is that correct?

DR. HARVIN: That's correct.

MR. SALTZMAN: In that case, I wonder if you can provide us any information on how you go about the setting up of the stability and control system; particularly, how you decide whether you are going to use offset rate or proportional control?

DR. HARVIN: Are you referring to the control of the solvent composition limits?

MR. SALTZMAN: I am talking about all the subsystems, for instance on the distillation apparatus--

DR. HARVIN: I can go through the control theories on the solvent recovery system. However, I am not from the Standard Gravure Corporation, so I cannot speak of their control of the composition or concerning how they use their ink, except for the fact that we know they do reuse it. There is a representative here from Standard Gravure who may wish to comment.

Regarding the control of the solvent recovery system, I mentioned the fact that the inlet air system has variable capacity control on the blowers. Therefore, regardless of the number of presses operating or the amount of effluent air, the system can accommodate that particular air volume through automatic duct pressure control. Thus, the system can always handle all the air that is being sent out or being used by the plant. In the event of an emergency shutdown of the solvent recovery plant, the solvent-laden air will automatically vent to the atmosphere.

The inlet air composition is measured and recorded by total hydrocarbon analyzers on the incoming airstreams. The outgoing composition is also measured and recorded. A composite sample of the effluent from the four active adsorbers is used. Just after the plant switches to a new drum, there is about a 5-ppm breakthrough. Then the breakthrough gradually rises to a predetermined set point, which is currently set at 14 ppm. When 14 ppm is detected by the analyzer, the system cycles. It usually slips on by about 15 ppm before it finally completes switching. When it switches over, a new drum comes on and the breakthrough goes back to about 5 ppm. So the effluent composition follows a sawtooth pattern.

As I mentioned, we avoided the use of distillation because Standard Gravure went to the use of a base solvent composition. Because of the way they operate with proofing operations, Spectacolor, and their regular gravure work, the solvent composition meanders but nevertheless stays within certain prescribed limits set up by Standard Gravure.

The laboratory people analyze the solvent on a regular basis. If they find that for some reason or other, due to the products they are producing, the xylol content is getting down a little bit, all they have to do is call up the ink manufacturer and tell him to go heavy on xylol in the small amount of solvent he must add. That will build up the xylol content of the inventory. Does that answer your question?

MR. SALTZMAN: Yes, I understand what you said. Thank you.

MR. WILLIAM H. BROWN (FMC Corporation, Marcus Hook, Pennsylvania): What steam to solvent ratios do you find typical in the adsorption cycle?

DR. HARVIN: This particular adsorption cycle is not the most efficient in the world because of the fact that the Standard Gravure people elect to operate a very low ppm value--400 to 500 ppm. So the loading of solvent on the carbon is relatively low, and the steam-solvent ratio is not the most optimum. Its range is between five and seven.

MR. BROWN: Thank you.

DR. HARVIN: That, incidentally, is something that is less subject to the design of your plant and more subject to the way you operate your plant. There are some solvents that can be recovered with ratios down in range of three, and other solvents that require much higher steam ratios. The steam/solvent ratio is more a function of the particular solvent system and the way a plant is operated than of the design equipment being used.

MR. KING: Thank you.

24 September 1975

Session IV:

IMPACT OF NEW DEVELOPMENTS AND CHEMICAL FORMULATIONS

Robert H. Downie*
Chairman

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*Vice President and General Manager, Research Division, Moore Business Forms, Inc., Niagara Falls, New York.

OPENING COMMENTS

Farley Fisher, Ph.D.
General Chairman

Our final session is on the Impact of New Developments and Chemical Formulations. It was with considerable pessimism that I originally accepted the idea that we should try to hold a session on new developments. My first reaction was, "Who is going to want to talk about something that they are trying to keep under their hats until they are ready to sell?"

I must say that I have been very gratified by the response from the industry. We do have a number of people here who are going to talk about some relatively new techniques and methods, which may offer real advantages from the point of view of environmental control.

SESSION INTRODUCTION

Robert H. Downie
Session Chairman

In looking at the speakers for this session, their themes, and their topics, I was impressed that this was only one of a group of people that we could have invited. These were not the sole four papers that we were able to garner from our industry, which showed new developments. When I looked at the papers, I tried to find some coherence in them. It struck me immediately that we are not looking at new developments here; we are looking at second- and third-generation solutions to problems that the industry recognized years and years ago. There is no new revelation being cast upon us in the graphic arts industry. There are some things wrong, and there are some things that could be better. What is typical of the papers and the developments that you're going to hear? These are not first-stab answers at correcting these problems. These are third- and fourth-generation answers to correcting them.

The unfortunate part from a profit point of view is that some of the first- and second-generation solutions that we came up with never did pay for themselves, other than by laying the foundation for the particular developments that we have now. In addition, there is absolutely no guarantee, as you well know, that the money that we are investing in current developments will be spent with successful results.

You are going to find that many of the developments were dictated by that wonderful disciplinarian, the marketplace. The American marketplace is a unique broth of ideas that is constantly burbling. I am always impressed at the way the weak and the unseemly and the nonmarketable get turfed out and at the correctness of things that persist, all without regulation and all with simply a discipline of what people want and are willing to buy. Every one of the developments that you are going to hear about today falls into this particular category. You will find strong evidence of creative and positive thinking on the part of the companies that are represented here and are willing to take you into their confidence, willing to show you what some of their advance thinking is.

I hope one of the benefits all of us will get out of this meeting is that we recognize the same problem, when we are through and identify them. EPA and industry must find a common theme and a common purpose. It is less than constructive if we do not get in the boat together, find out how we can exploit new solutions and developments, and bring them to their optimal, not their idealistic, marketing value.

UV AND OTHER METAL-DECORATING PROCESSES

Elgin D. Sallee*

Abstract

Inks used in metal-decoration are not significant sources of emissions since they contain essentially no volatiles. The conventional organic solvent-borne surface coatings used in conjunction with metal-decoration, however, are important potential sources of hydrocarbon emissions. The preferred control measure for such emissions is reformulation of the surface coating to eliminate, reduce, or alter the volatiles content. Where this is not feasible, emissions are incinerated, using natural gas or LPG as auxiliary fuel. Incineration is relegated to last resort action in view of the extremely critical fuel supply situation. This paper describes fuel-savings features of solvent vapor incineration systems, as well as the environmental concerns in selection of chemicals used in formulation of UV-curable and other solvent-free or low-solvent materials for metal coating and decorating.

In discussions of the environmental concerns involved in any manufacturing process, the first item of significance is the quantity of materials used. In attempting to total metal-decorating materials, confusion is encountered from the outset because of varying definitions of metal decorating. Many of those who are experienced in the business call metal decorating any process in which a colorant is applied to the metal surface. This would include paint, enamels, inks, and even those varnishes, lacquers, or shellacs that impart color to the metal surface.

Others regard metal decorating as only those processes in which ink is printed on the metal by means of an offset or lithograph press. Yet in some instances such equipment is used to apply ink uniformly over the entire metal surface. Some people call this application surface coating rather than metal decorating. Ordinarily only a specialist in the business would be able to tell whether the dried, uniformly colored surface had been printed with an ink or whether an enamel of the same color had been applied by a roller coater machine.

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*Director of Environmental Sciences, Corporate Environmental Affairs, American Can Company, Greenwich, Connecticut.

Many of the ingredients of inks and surface coatings are similar. There are also close similarities in the environmental concerns and control measures involved. Metal surface coating is frequently considered ancillary to metal printing; both done in the same manufacturing room, and sometimes on the same manufacturing line with both materials dried simultaneously in the same oven.

Accordingly, my comments include metal-decorating inks and coatings as separate items for those processes and materials now in large-volume use, as well as some of those involved in new technology.

The can-manufacturing industry is by far the major user of inks printed on metal. To my knowledge usage in industries other than can manufacture amounts to less than 1 million pounds annually, whereas ink for metal cans made in this country amounts to about 15 million pounds per year. Currently, about 90 percent of this ink is printed on metal sheets before the sheets are cut to size and formed into cans; the remainder is printed on formed can parts. Inks are for the outside surfaces only.

Currently about 85 percent of the metal-sheet-printing ink is the conventional thermally cured type applied in about equal proportions by the dry offset printing process and the wet lithographic process. These inks are of the same general type, and environmental aspects are the same for both printing processes.

Figure 1 is a schematic of the typical conventional ink application and drying process. It depicts the printing press with the printed sheets moving into the drying oven where they are picked up by supports (called wickets) on a continuously moving chain, which carries them through the oven with exposure to uniform temperature of 330° to 350° F for about 6 minutes. The lower part of the oven (empty wicket chain return section) is sealed off, except at entrance and exit, from the upper part through which the printed sheets move. Uniform temperature is maintained in the oven zones by the circulation of large volumes of air heated by gas burners. A comparatively minor proportion of the circulated air is drawn from each oven zone, so there is general air movement toward the oven exhaust stack. Fuel combustion products as well as any materials volatilized in the oven are exhausted at this point. The returning empty wickets must be heated just before they pick up the printed sheets; otherwise the quality of the printing is affected. Ink usage rates vary, of course, with the area of surface printed and thickness of the ink film applied. Typically, it may be as little as 0.1 lb/hr per color, or, in the case of a heavy white ink covering the entire sheet, as much as 35 lb/hr.

Table 1 gives general information on the composition of conventional, heat-cured metal-printing inks. Note that the extent of vehicle or resin in individual formulations may vary widely dependent on the extent of colorant and extender (the extender is primarily for dilution of the colorant). Some inks require no extender, dryer, or solvent. All inks printed on metal are commonly termed as free of volatiles. This is not absolutely true, since any free solvent is driven off in the oven along with any volatiles released in the resin polymerization. At most, however, the extent of volatiles from the latter amounts to 3 percent of the resin. Typical volatiles content of the ink is less than 1 percent, with a maximum of 3 percent.

Accordingly, emission problems involved in application of conventional thermally cured ink for metal are practically nonexistent. Ordinarily no emission-control devices are required for the oven exhaust if the process involves use of ink only.

However, in the major proportion of printing on metal (in my company about 70 percent) the printing is followed by a tandem roller coating of solvent-borne varnish. In most instances this overprint varnish is applied over the wet ink, as shown in figure 2. Both the ink and the varnish are oven-dried simultaneously. Were it not for the varnish, emission control problems in the use of metal-printing ink would be essentially nil.

I mentioned previously that currently about 85 percent of metal-printing ink is the conventional heat-cured type. Essentially all of the remainder is the ultraviolet-cured type. Use of UV ink has no marked advantage (or disadvantage) over conventional inks with respect to emission control, since neither contains a significant extent of volatiles. Use of UV ink with conventional tandem roller coating of overprint varnish, as shown in figure 3, still requires use of an oven for the varnish. This process is ordinarily the first phase in the development of technology for use of UV curable materials. This arrangement does have a distinct advantage in savings of fuel gas in those situations where the ink must be dry before varnish is applied. With inks that must be dry before varnishing, the figure-3 arrangement eliminates one pass of the metal sheets through the gas-heated oven. BTU's required for UV curing are about one-tenth of those for gas-heated oven operation.

Application of varnish or of any organic solvent-borne roller coating on metal involves obvious emission control problems. Measures to counteract these include reformulation of the coating to eliminate or reduce extent of solvent content, or change to preferable solvents, such as less photochemically reactive types, or incineration of the oven exhaust. Other types of emission control devices, based on adsorption, absorption, condensation, scrubbing, chemical oxidation, electrostatic precipitation, or a combination of these principles, have been evaluated thoroughly and found inadequate or impractical except in rare instances. Where an emission control device is necessary, incineration is almost invariably the only dependable control technology. Particularly because of the fuel supply situation, use of incineration is relegated to last resort action. Where there is no practical alternative to incineration, it is essential to do it with minimum fuel consumption.

Figure 4 is a schematic of a typical sheet-coating operation. Basic equipment is similar to that for roller coating of varnish illustrated previously, except that the oven for drying enamels and lacquers is usually larger to accommodate greater usage rates of material. Typical solvent vapor emission rates from a print-varnish oven are 40-80 lb/hr, whereas a modern coater oven may emit as much as 200 lb/hr.

Figure 5 depicts a roller coater unit with "straight-through" incineration of the oven exhaust air. This consumes vast quantities of fuel gas.

To reduce fuel consumption, various arrangements of catalyst systems, heat exchangers, and heat-recovery systems, or a combination of these, are used. Figure 6 is a schematic for a catalytic incineration system showing typical temperature measurements.

Figure 7 traces the route of oven exhaust through a heat exchanger and a thermal incinerator and typical temperatures involved. Figure 8 shows an arrangement of heat exchanger, burner, and catalyst unit, and figure 9 the same kind of arrangement but with the addition of heat recovery.

In most instances, particularly in can-manufacturing plants, it is not possible to make practical use of heat discharged from such systems for other than the litho-coating process itself. This, of course, depends on circumstances. Most solvent vapor incinerator systems are add-on installations made long after the plant was constructed. Possibly for a new plant, beneficial use of heat discharged from such control devices can be designed into the plant for space heating or for processes other than heating the litho-print or coater oven itself.

Figure 10 depicts a system used extensively in my company. Incinerator discharge air is ducted to the various heating zones of the oven, replacing burners for the oven zones and wicket preheat section.

At best, all solvent vapor incineration systems consume some fuel gas. Under present circumstances it is preferable to change to use of coating materials that obviate need for emission control devices. This, however, is much easier said than done. Successful reformulation of coating materials used by can manufacturers is a tremendous task, particularly for those coatings used for can linings.

Table 2 lists the most common ingredients of conventional solvent-borne can coatings in decreasing order of volume usage for the respective types of ingredients. Several others of each type ingredient are actually used, but extent of such usage is comparatively small, their total combination amounting to less than 10 percent of the respective total. Except for varnishes, most such coatings contain no drying oils. The majority contain no additives. Lubricants most commonly used are silicones or wax. Various combinations of the resins listed may be used in an individual formulation. Some coatings may contain only one solvent, such as mineral spirits; others may contain as many as 10 different solvents.

The effort to reformulate to low-solvent or no-solvent coatings is complicated by the wide variety of coating material end uses and resultant physical requirements. Well over 600 different coating material formulations are used in the can-manufacturing industry. My company routinely uses more than 300 formulations of solvent-borne coatings. Some of our individual plants use as many as 90 different formulations annually.

The important criteria for all coatings used in can manufacture are summarized in table 3. This list is an oversimplification of the concerns involved. A formidable amount of investigative work goes into the successful development of each new coating material. The formulating laboratory, despite long experience and knowledge of the chemical and physical properties of the various individual ingredients, ordinarily compounds and tests a great many formulations before deciding on one considered sufficiently promising to warrant submitting samples to the user. The user or can manufacturer then subjects the new material to a gamut of testing with emphasis on freedom from difficulties and hazards in application and use of the material and assurance that the material will do the job intended with respect to maintaining quality of end-use product. The latter includes packing the customer's product in the cans and examining it after varying storage and abuse conditions.

Toxicity of the coating material, of course, is of primary importance. Where toxic properties of the ingredients and formulated coating are not already known, this must be evaluated carefully. The materials must be relatively nontoxic to can-plant employees, plant neighbors, can packers, and to anyone involved in the product-distribution, product-consumer, and container-disposal and -recycling system. Screening information (tests on animals) must be made available for toxic effects through ingestion, inhalation, and skin absorption, as well as tests for eye irritation and determination of whether the material is a primary skin irritant. Such information is required on individual ingredients as well as the compounded formulation. Where screening-test information indicates potential for adverse effects, further detail is required, such as potential chronic toxicity information and hazard-control detail.

Closely allied to toxicity detail is knowledge of the volatility of the ingredients and the formulated material, with respect to protection of our plant employees and control of emissions. Fire hazard and any nuisance or physical hazard to employees or facilities are also important considerations.

Stability of the material is important. It must not change during transportation and storage at our plant. Otherwise, troubles might be encountered in use of the material in can-manufacturing processes, or adverse effects might be encountered by our customers or ultimate consumers.

Applicability of a new formulation is extremely important. It must be free of significant problems in application to the metal surface, drying the coated film, and fabrication of the coated metal into containers at high production rates. The dried film must not be affected during storage and transportation and must cause no difficulties to the customer in filling, sealing, and processing the filled containers.

The prime requisite of the container is its integrity; it must provide required shelf life for the canned product and preserve its quality. No detectable portion of the coating material can leach or migrate into the canned product. Flavor, odor, and texture of the product must not be affected.

If a new resin system, one that does not have prior Food and Drug Administration sanction, is used in a coating formulation for lining of cans for edible products, then lengthy extraction and animal-feeding tests are required. The usual time required for these is 2 to 4 years at costs now exceeding $500,000 for each new resin system.

The standard procedure for evaluation of a new coating material submitted to the can manufacturer involves laboratory examination followed by plant trial use, fabrication of about 1,000 cans, filling them with the customer's product, and periodic examination after storage. If the material passes all requirements, then larger quantities are fabricated, packed, examined, etc. Usually, progression in three stages to the million-can quantity is required before customer approval for use of the new coating formulation in commercial quantity is obtained.

Obviously, availability of the new coating formulation at practical cost is essential. Otherwise, it would be better to continue with conventional time-proved materials with provision of the control devices for the emissions.

New formulations can be rejected for failure to measure up to standards for any of the foregoing criteria. The track record for new formulations attests to the difficulties involved. In my company's experience an average of 3 of 100 candidate materials submitted by coating-material suppliers eventually reach the commercial use stage.

Appreciable success is being attained in reformulating to water-borne varnish and various other surface coatings for metals. A relative few of these contain no organic solvent, but in most of those now in commerical use, the volatile portion consists of 20 percent organic solvent and 80 percent water. With some materials prohibitive troubles are encountered if the organic solvent portion of the volatiles is lower than 30 percent. The most commonly used organic solvents in water-borne coatings are cellosolves and butyl alcohol.

Comparatively amazing success has been realized in development of UV curable inks. There is good promise that this will continue and that this experience will enhance success in development of UV curable surface coatings for metal.

Table 4 lists the kinds of ingredients in UV metal-decorating materials (coatings and inks) now showing considerable promise. There are many variations, of course, in choice of these components and concentrations involved in individual formulations. At the moment, apparently most progress is being made with acrylate systems (free radical cure systems), but significant progress is also being realized with cationic, two-package epoxy formulations. Of prime importance in the development of UV materials is the requirement that volatility of the material be closely limited. This must be controlled by specification. It is essential for protection of can plant employees as well as prevention of emissions to the extent that no emission control devices are required.

Figure 11 illustrates UV ink application by tandem presses, each followed by a UV drying system. In most such arrangements each press may apply two colors of inks. These are followed by application of water-borne varnish which requires no emission control device for the oven exhaust air.

The typical UV curing unit has two exhaust ducts handling a total of about 3,000 CFM. This is for exhaust of air for cooling of the UV lamps, the ozone they generate, and any monomers or oligomers volatilized during the UV cure. As mentioned, extent of the latter is limited by specification. My company rejects UV-curable material formulations if the volatiles result in emissions greater than 0.5 lb/hr. Ozone evolved and exhausted to the atmosphere varies with power of the lamps, but never exceeds 1 ppm in the exhaust air or 0.02 lb/hr.

Even though hydrocarbon emission problems are resolved through use of UV inks and water-borne coatings, fuel gas consumed by the drying oven for the latter, or for high solids content solvent-borne coatings, remains as a critical problem. Accordingly, progress is being made in development of UV roller coatings. With these the figure-12 schematic of process equipment is used, and the gas-heated oven is eliminated.

Although my comments have been on decoration of metal sheets before fabrication into cans, technology developments in decoration and coating of formed cans are keeping pace. We expect continued rapid growth of UV materials in the metal-decorating industry, with major replacement of thermally cured materials in only a few years. My company, for example, currently has 17 metal-decorating lines equipped with UV units in commerical use. Eight more will be using UV materials by mid-1976. By 1980 we anticipate that all of our metal printing and half of our metal coating will be with UV materials.

(On the following pages are the 4 tables and 12 figures cited in the text.)

Table 1. Conventional (heat-cured) metal-decorating ink

Component	Percent
Low-viscosity resin (e.g., oil-base alkyd, epoxy ester)	30 to 95
Pigment or colorant (e.g., cobalt blue, iron oxide, earth colors, organic dye coprecipitated with aluminum hydroxide, titanium dioxide)	5 to 60
Extender (e.g., aluminum hydroxide)	0 to 50
Dryer (e.g., cobalt naphthenate, manganese naphthenate)	0 to 0.2
Solvent (e.g., high-boiling mineral spirits)	0 to 1.0

Table 2. Conventional solvent-borne roller coatings for metal sheets

Resins	Solvents
Vinyl	Aliphatic petroleum hydrocarbons
Epoxy	Methyl isobutyl ketone
Alkyd	Methyl ethyl ketone
Phenolic	Glycol ethers & ether esters
Polybutadiene	Xylene
Oleoresinous	Butyl acetate
Polyester	Butyl alcohol
Acrylic	
Amino	
Additives	**Drying oils**
Titanium dioxide	Linseed
Aluminum powder	Cottonseed
Zinc oxide	Soya
Lubricant	Coconut
	Safflower

Table 3. Criteria for metal-decorating material

Toxicity	Stability	Integrity
Volatility	Applicability	Availability and cost

Table 4. Ultraviolet-curable metal-decorating materials

Component	Percent
Vehicle (e.g., bisphenol-A epoxy diglycidyl ether, trimethanolpropane triacrylate, urethane, 2-package epoxy systems)	40 to 90
Photoinitiator or photosensitizer (e.g., bisphenol, Michler's ketone, Lewis acid)	
Accelerator (e.g., methyl diethanolamine, other tertiary amines)	1 to 6
Stabilizer (e.g., benzoquinone)	0 to 1
Additives (e.g., wax, silica gel)	0 to 5

NOTE.-The above materials are typical of those used in UV varnish. They are also typical of those used in UV inks containing up to 50 percent pigment.

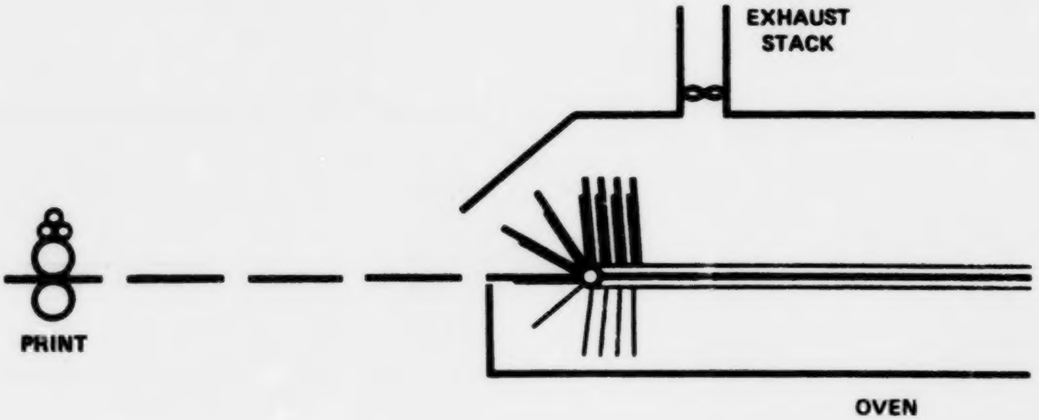
EXHAUST STACK
PRINT
OVEN

Figure 1. Metal sheet decorating unit conventional heat-cured ink.

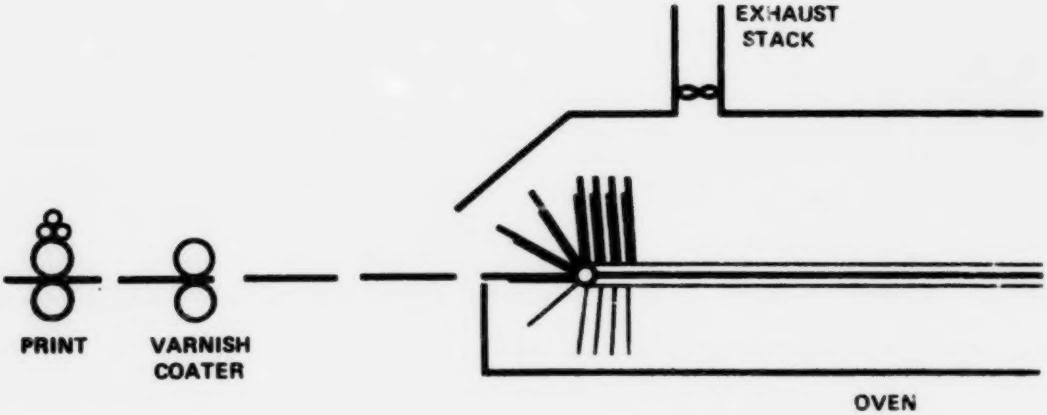
EXHAUST STACK
PRINT
VARNISH COATER
OVEN

Figure 2. Metal sheet decorating unit using conventional ink and solvent-borne varnish roller coated over the wet ink.

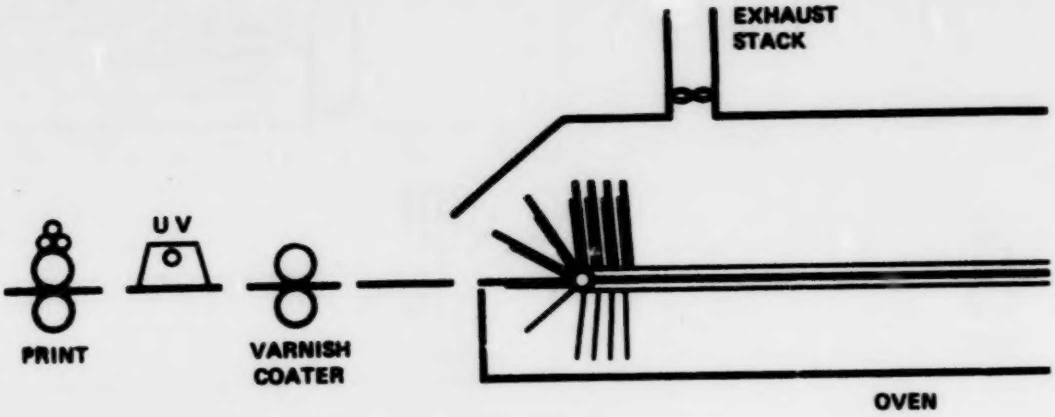
EXHAUST
STACK
UV
PRINT
VARNISH
COATER
OVEN

Figure 3. Metal decorating unit using ultraviolet curable ink and solvent-borne overprint varnish.

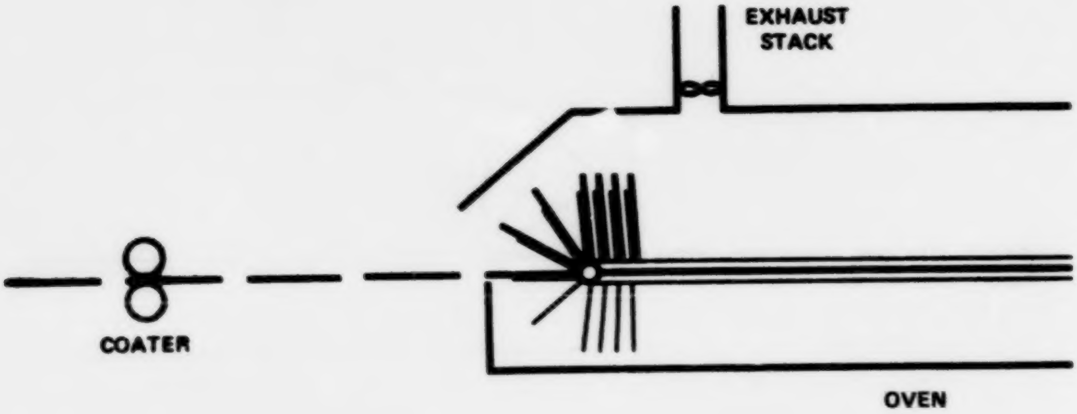
EXHAUST
STACK
COATER
OVEN

Figure 4. Metal sheet roller-coating with solvent-borne enamel, lacquer, sizing or varnish.

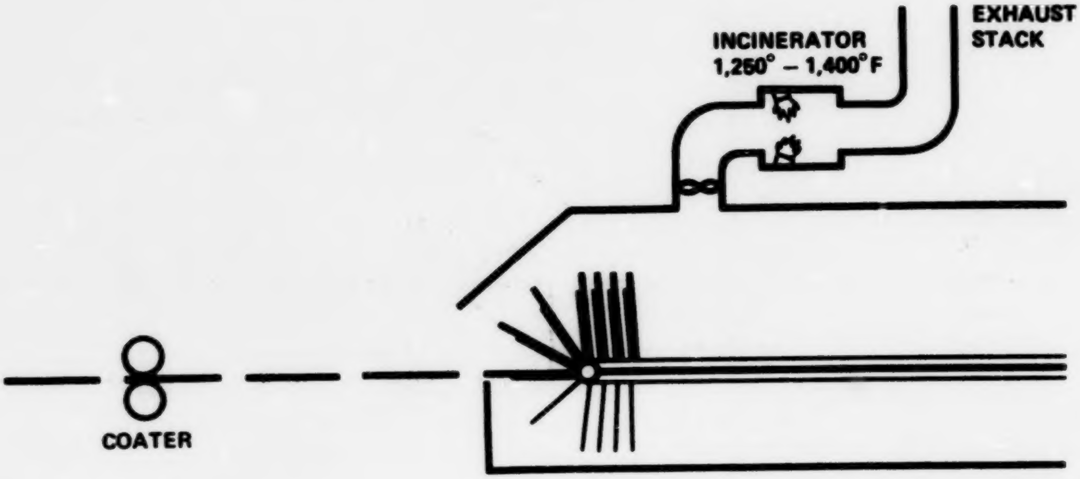
INCINERATOR
1,250° – 1,400°F
EXHAUST
STACK
COATER

Figure 5. Roller-coater unit with thermal incinerator for oven exhaust.

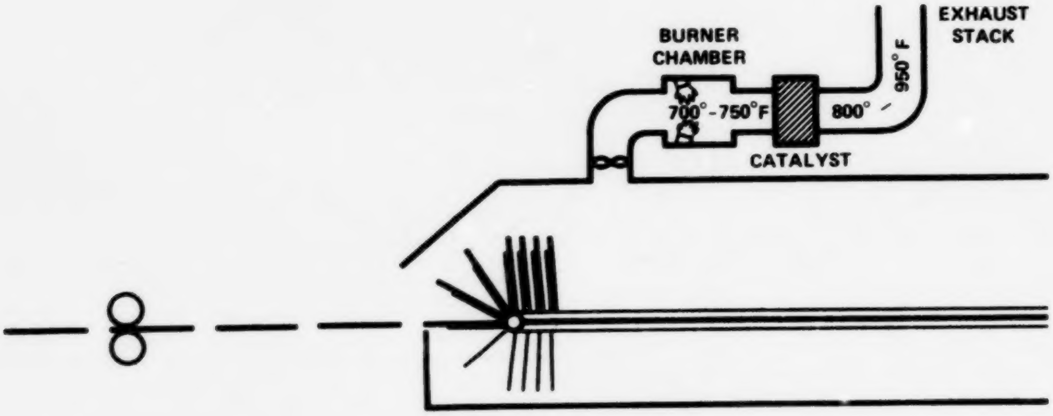
BURNER
CHAMBER
700°-750°F
800°
950°F
EXHAUST
STACK
CATALYST

Figure 6. Coater unit with catalytic incineration system.

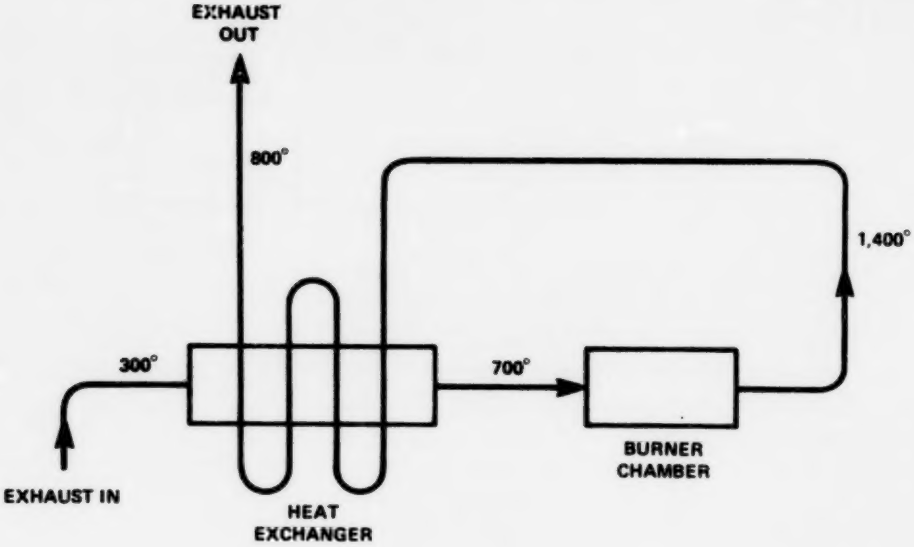
EXHAUST OUT
800°
1,400°
300°
700°
EXHAUST IN
HEAT EXCHANGER
BURNER CHAMBER

Figure 7. Thermal incinerator with heat exchanger.

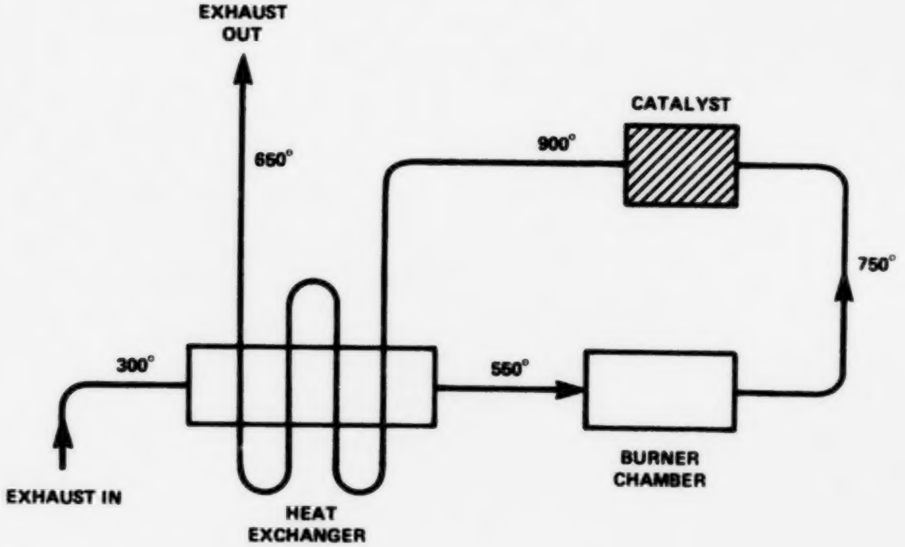
EXHAUST OUT
CATALYST
900°
650°
750°
300°
550°
EXHAUST IN
HEAT EXCHANGER
BURNER CHAMBER

Figure 8. Catalytic incinerator with heat exchanger.

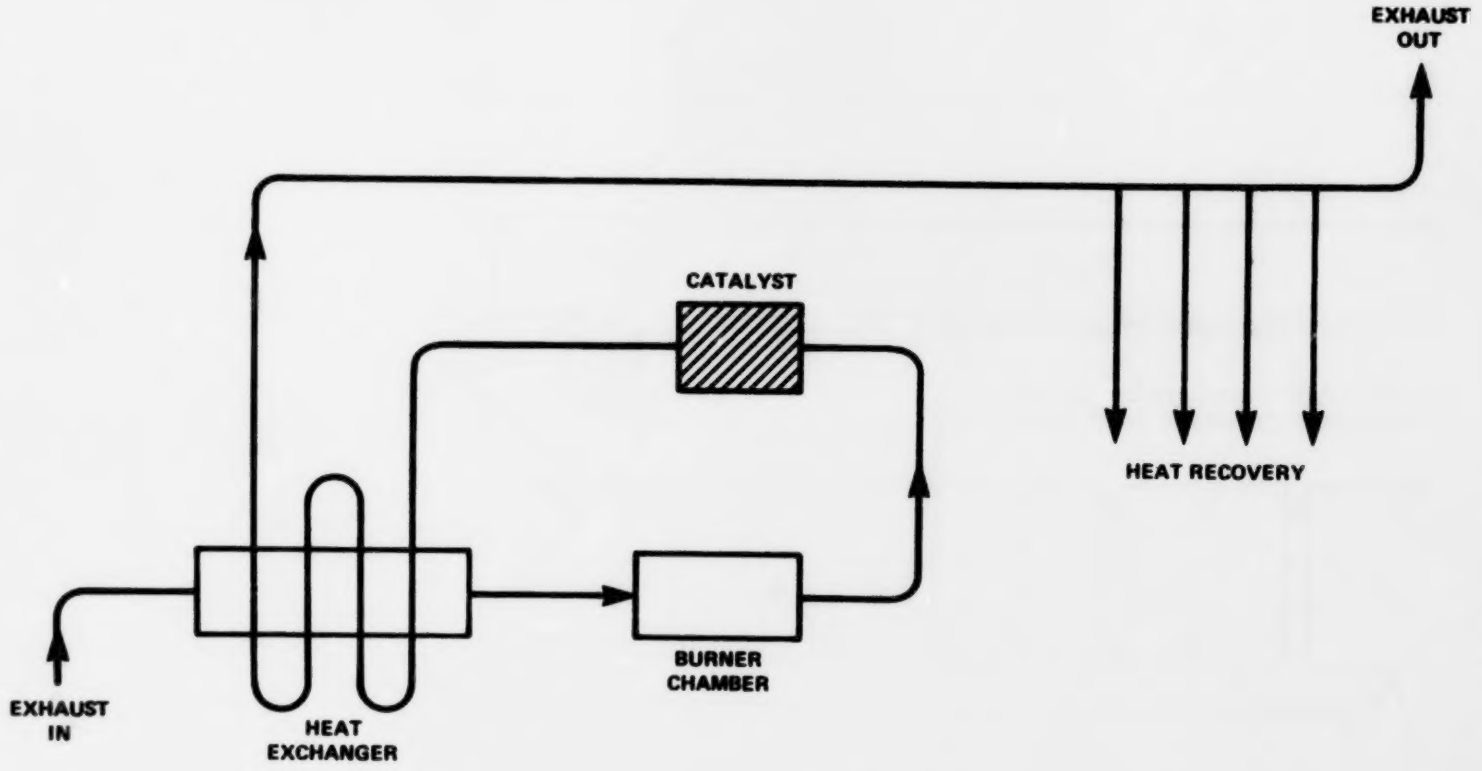
EXHAUST
OUT
CATALYST
HEAT RECOVERY
EXHAUST
IN
HEAT
EXCHANGER
BURNER
CHAMBER

Figure 9. Catalytic incinerator with heat exchanger and heat recovery.

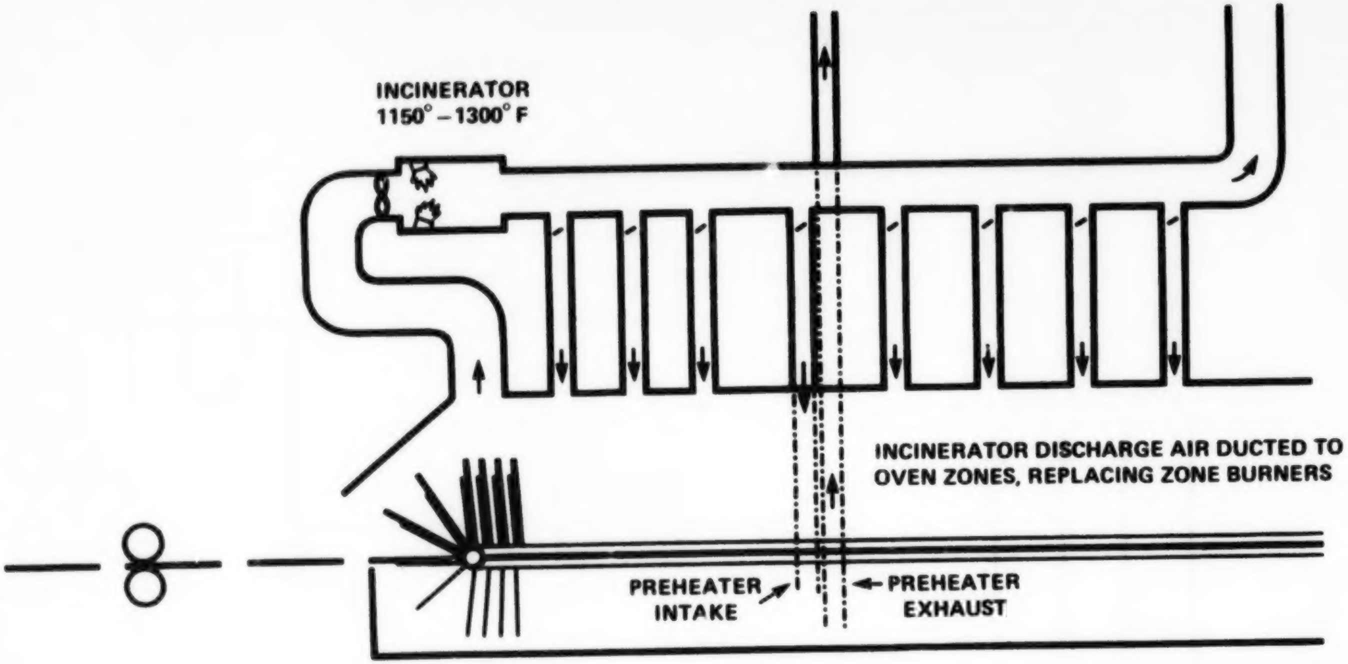
INCINERATOR
1150° – 1300° F
INCINERATOR DISCHARGE AIR DUCTED TO
OVEN ZONES, REPLACING ZONE BURNERS
PREHEATER
INTAKE
PREHEATER
EXHAUST

Figure 10. Thermal incinerator with heat recovery.

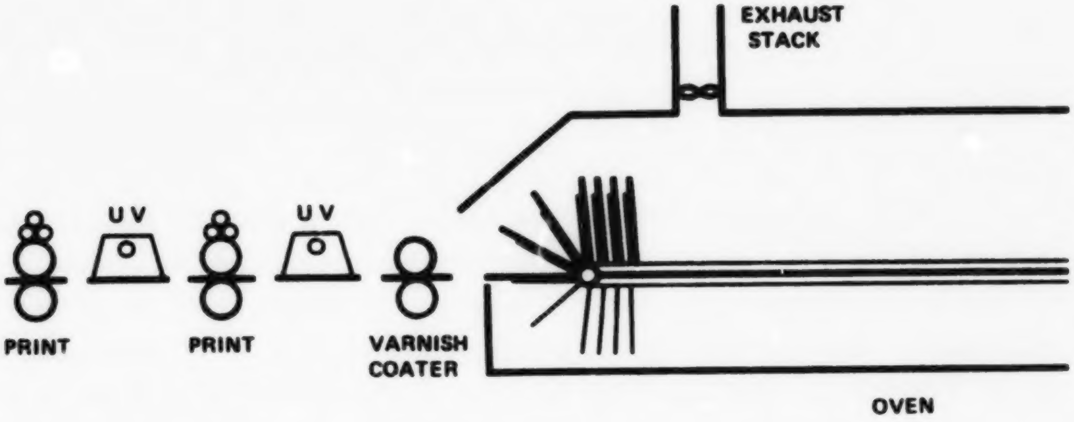
EXHAUST
STACK
UV
UV
PRINT
PRINT
VARNISH
COATER
OVEN

Figure 11. Tandem UV printing units followed by solvent-borne varnish.

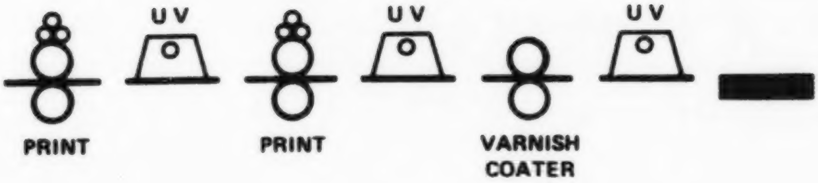
UV
UV
UV
PRINT
PRINT
VARNISH
COATER

Figure 12. Tandem UV printing followed by UV varnish.

THE APPLICATION OF SOLVENTLESS INKS IN WEB AND SHEETFED OFFSET SYSTEMS

W. E. Rusterholz*

Abstract

A brief history of solventless ink systems introduces this review. The factors that have led to the current usage of ultraviolet curing systems in web and sheetfed offset printing are presented. A survey of the advantages and disadvantages of these ink systems is made with relation to this segment of the printing industry. The roles of energy, pollution regulations, and economics as motives for using solventless inks are discussed. Finally, the estimated $4,000,000 market for 1975 is broken down by end-use applications.

No one can argue that the concept of a solventless ink system is not timely; and it is certainly not new. In fact, it has its roots in the traditional mechanisms associated with the method by which a printed ink film is immobilized. These methods are: 1) Oxidation (chemical), 2) Penetration, 3) Solvent evaporation, and 4) Moisture setting (precipitation). There is no doubt then that a news ink is a solventless system since, it is a dispersion in essentially nonvolatile liquid carriers that set by absorption into the pulpy news stocks, which function like a blotter. In the same sense, many traditional sheetfed inks are also solventless systems, being dispersions in nonvolatile oleoresinous vehicles. These cure in time by oxidation.

Today most people feel that solventless inks were developed to replace conventional heat-drying offset inks. High-speed web offset has been one of the largest growing segments of the converting industry since the 1960's. At about this same time, concerns for the environment with regard to air pollution were growing with equal vigor. It was already obvious in the mid to late 1960's that this expanding market was on a collision course with the environmental legislation.

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*Manager, Technical Support Section, Sun Chemical Corp., Carlstadt, New Jersey.

The heart of the conventional offset heatset ink formulation is a low-molecular-weight resinous binder dissolved in a proprietary hydrocarbon solvent blend. Standard formulations utilize up to 35-40 percent by weight of these hydrocarbon solvents to impart the flow properties necessary in the printing process. The setting of the ink film is then accomplished by removal of most of the hydrocarbon solvents by evaporation. The low-molecular-weight resin is regenerated and forms the binder of the dry, pigmented ink film.

By the early 1970's the models for the current air pollution regulations were hitting hard at these same hydrocarbons as a major source of organic pollutants. In addition the concept of first dissolving and then regenerating heatset resins was recognized as an energy-expensive procedure. On one hand there is use of energy to effect solution, and very high energies (1,000,000 Btu/hr) associated with common gas-fired heatset ovens are used to evaporate the solvent from the printed film.

One solution to heatset solvent emissions in the late 1960's and early 1970's was the afterburner. This energy-wasteful device became less feasible by 1973 as natural-gas shortages developed. By 1974 it was a hard fact of life that severe gas shortages were threatening the gas previously allocated to standard web, offset oven operations; to this must be added the well-remembered chemical raw materials shortages of 1974. The stage was set for the entrance of the solventless ink alternative.

Over the past 10 years, the major ink producers have committed increasing percentages of their research dollars to solventless ink development. This technology evolved through a series of steps paced by the confining restraints of pollution, energy, and, finally, cost. As these factors came into play, the solutions ranged from exempt solvent formulations to high-resin solids and low solvent content and, finally, to no solvent. All of these alternative systems are available today.

Solventless inks can be thought of as ones in which the high-molecular-weight resinous binder is formed immediately after printing. These can be roughly divided into systems initiated by heat or by higher forms of energy.

The thermally curing solventless system is based on the copolymerization of a blend of liquid synthetic resins. The reaction is initiated by a latent catalyst present in the one-pot system, which is triggered by the heat of a conventional heatset oven. The advantages of the system are good gloss and excellent film properties, and, especially, rub and grease resistance. The disadvantages are chiefly costs. Some effluent is also liberated because this is a condensation polymerization that, depending on the raw materials used, evolves water, lower alcohols, and trace organics such as aldehydes. With inks of this type, it was possible to approach an 85 percent reduction in emissions with no hydrocarbon effluents.

Considering the history of printing ink technology, heat-catalyzed systems with these advantages should have been a major development. However, the rapidly changing influences of the critical factors mentioned previously virtually obsoleted these systems due to their poor economics and to their reliance on gas-fired drying equipment.

At present, solventless ink technology has turned to more energetic types of drying. The three areas that have been most intensively investigated are microwave, electron beam, and ultraviolet radiation. The microwave technology is restricted to ink systems with high loss factors which limits its present use to water-base vehicles. Electron beam offers advantages of curing thick films (greater than 1 mil), but this technology has been applied only in the coatings area to date. Ultraviolet curing has gained wide acceptance in printing because it offers an acceptable compromise of an easily shielded, reasonably high energy radiation from available sources at a reasonable cost.

The ink systems commercially used in both web and sheetfed offset printing are composed of liquid nonvolatile monomers and prepolymers combined with a photoinitiator. When the composition absorbs UV light, the photoinitiator is activated and a rapid crosslinking reaction occurs. Since this reaction is based on an addition polymerization, no effluent at all is liberated from the ink during the drying (curing) period.

The main advantages of UV to web printers have been:

1. Lack of pollution,
2. Excellent stability on the press distribution system,
3. Independence from gas-fired equipment,
4. Less substrate degradation than in conventional heatset ovens.

The advantages to sheetfed printers are somewhat different. Since sheetfed has essentially always been a solventless process, the lack of pollution is not the incentive. It is here that the enhanced film properties of UV-cured inks most often account for its usage. The advantages are that:

1. The instantaneous film properties allow work and turn in production,
2. Offset spray is eliminated,
3. Secondary in-line processing becomes possible (die cutting).

The disadvantages of UV curing are the same to both areas of usage. These are:

1. The higher cost of inks due to replacement of solvent with high-cost monomers,
2. The purchase of new "drying" equipment,
3. Difficulty of deinking fully cured prints by conventional methods,
4. More sophisticated safety requirements in handling the uncured inks.

The question of safe handling of UV systems is an important one. At present most commercial UV inks are based on acrylate chemistry. In comparison to conventional ink vehicles, acrylates have a higher intrinsic toxicity associated with them. They are irritants to the eye, and most are rated as potential skin irritants by standard testing procedures.

As UV solventless inks have moved into commercial usage, an effective exposure reduction program for the pressroom is essential. Prescreening of commercial ink vehicles for skin irritation potential provides a sound approach to reduce hazards. In practice the exposure reduction program for offset pressrooms is a fairly simple one and represents a second-line precautionary measure.

It has been found that the biggest single obstacle to lowest practical exposure at the converting level is a worker's own past experience. This is because conventional offset inks use raw materials of very low inherent toxicity, even at very high dose rates. An effective safety program usually stresses a reeducation to good commonsense work habits at both the worker and supervisory levels.

To put the present picture in perspective, the printer has a series of restrictions that are driving him away from his traditional technical and business posture. The ink industry has sought alternatives that can offer both immediate and, hopefully, longer term benefits. The degree of acceptance of solventless systems into the web or sheetfed markets results in a series of trade-offs by the individual converter to balance his particular needs.

1. Utilities vs. Agencies: On one hand, there is pressure to eliminate pollution by incineration, but on the other, many converters can have no new gas allocations and even face cutbacks on existing equipment.
2. Print Quality--Solventless Systems vs. Conventional: The individual converter's product mix requirements affect his need to choose between such things as improved printing sharpness and improved film properties at nearly equivalent gloss of conventional inks.
3. Benefits vs. Economics: On ink cost alone UV is certainly not justified. The current pricing on web UV process colors averages a 100 percent upcharge over conventional. For black a 200 percent upcharge is usual because of the relatively low price of conventional black inks.
4. Enforcement vs. Competitive Position: The equitable enforcement of pollution regulations is necessary to prevent removal of work from one plant to another or one competitor to another because of the converting costs. The ultimate solution to inequitable enforcement has been the relocation of plants and its attendant dislocations in employment.

With this perspective it is worth noting that the estimated dollar market for UV paper applications will approach $4,000,000 for 1975. At mid-1975 this market was based on the following distribution of press installations:

40 web presses printing envelopes, catalogs, magazines, books, etc.,
15 sheetfed presses printing cartons,
20 sheetfed presses printing labels, brochures, book jackets, etc.

In summation, it can be said that conferences such as these can provide a forum for both the government and the printing community to exchange viewpoints. It would seem that the greatest danger to all of us is to be precipitous in our actions. It is necessary to have the time to develop sound technology in response to what is reasonable to achieve, and all of this must fit some reasonable economic framework.

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ELECTRICURE* ENVIRONMENTAL IMPACT

Robert G. Muggli, Ph.D.†

Electricure electronic systems' effect on the environment inside and outside a printing plant is total. The ultimate environmentalist objective of zero pollution is now completely realizable. As are other electronic devices, Electricure electronic systems, are compact, sophisticated, precisely controllable, quiet and instantaneous in operation, energy conservative, and a quantum leap ahead of conventional methods. Their use in the printing industry becomes a question of "when," not "if," once Electricure systems are understood completely. The scope of this presentation does not permit their uses, however, so those concerned are encouraged to examine references 1, 2, and 3.

Briefly but systematically, I would like to describe Electricure electronic systems and their "impact" on the environment and on the printing industry.

Electri Graphics

EGI is concerned with complete production systems designed to utilize emerging electronic technology to the optimum. We abandon laboratory devices to those with lesser objectives. Our reasoning is that the industry problems of energy, pollution, cost, petroleum shortage, and OSHA standards are here with us now, and need to be solved now. Research conducted to prove that which is already known, as is depicted in the cartoon, "Research is what we do to prove what we know," does not make progress now. Thus we will leave this area to the nonpragmatist. In Chicago, we have entertained many researchers, only to learn later that they have rediscovered what they had already seen and heard at EGI!

Electron Accelerators

For over 20 years, electron microscopes, cathode ray tubes, electron beams, and electron curtains have been in use for various purposes: research, entertainment, vulcanizing of rubber, curing of plastics, coatings, etc. Electricure electronic systems employ electron acceleration, and our recent developments impart the industrial reliability needed. A precisely defined, uniform, continuous, high-energy electron discharge of any width is maintained constantly and is automatically controlled. The principal of operation is basically simple: electrons available from incoming power lines are raised a thousandfold in potential by a transformer-rectifier network encased inside power supply modules. Cable transmission is made to the accelerator, where this energy is shaped and projected outwardly, lengthwise of the tube, at the product (web, sheet, item, etc.). The quantity is regulated or slaved to the press, thus eliminating the need for a Ph.D. to operate a system (my job security seems to be on a limb).

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*Electricure is a trademark of Electri Graphics, Inc., Chicago, Illinois.

†Technical Director, Electri Graphics, Inc., Chicago, Illinois.

Process Environment

The atmosphere within the process zone is reduced by the energetic electrons emitted from the accelerator, thus preventing the formation of ozone and eliminating the need for nitrogen blanketing.

Chemistry

Electricure inks, coatings, and adhesives are real-time examples of quantum concepts of chemistry: orbital states, energy transition, etc. They are stable, nonvolatile, nonflammable, nontoxic, liquid, and semiliquid compositions prone to instant solidification when energized by high-speed electrons.

Air Pollution

Electricure electronic systems offer an alternative to afterburners, smoke precipitators, solvent incinerators, solvent recovery plants, and air contamination. Cold ovens without exhaust piping, drying without heat, and ink without solvents are Electricure precepts. The elimination of pollution is complete: no thermal pollution, no solvent pollution, no combustion fumes, no noise pollution.

Solvents

The amount of solvent in conventional inks varies from a small quantity to over 75 percent. The process of ink drying by evaporation of these solvents causes air contamination of press rooms and the surrounding environment. The storage of large quantities of solvent presents major fire hazards, as both Chicago and Philadelphia have experienced. Electricure electronic systems make these problems characteristic of a bygone era. Petroleum usage is further reduced as less frequent washups are required. Elimination of premature ink drying on the press is axiomatic because Electricure inks can only be dried by high-energy electrons. A further coorelative is that the liquid inks with complete press stability can be printed with thinner, more pigment-concentrated films, thus saving on chemical usage. Similarly, the constant addition of solvent on a press in order to maintain viscosity vanishes with this new technology.

Press Speeds

Electricure ink drying speed is measured in milliseconds. Unlike conventional drying where press speeds are limited by the drying capacity of the ovens, Electricure electronic systems are limited by the speed capability of the press. This reverses the historic dependence on drying-time considerations in printing.

Press Design

Because of their compactness, Electricure electronic systems permit the design of smaller, but faster presses. With 100 percent stable inks, automation of press operations is possible, freeing people from mundane operations, such as removing dried ink from rollers, plates, and cylinders; doctor blade adjustments; solvent additions; ink addition; and the numerous other details a pressman must attend to in order to keep printing with inks that dry everywhere, as well as in the oven.

Pressrooms

A pressroom with Electricure electronic systems can be ideal. It would be air conditioned and brightly lighted with small compact presses without exhaust systems, heat, smoke, fumes, or fire hazards--a modern illustration of an industrial plant designed with people in mind and for sharp contrast to contemporary pressrooms.

Print Quality

Instantaneous, cold-energy ink drying produces copy that is sharper and more vivid; has higher gloss, increased durability, and more skuff resistance; and possesses higher consistent color fidelity than any prior method of ink drying. A few researchers have contrasted Thermal, UV, and Electricure quality of printing and have confirmed the fact that Electricure inks are, in all aspects, unmatched.

Cost

The capital cost of Electricure electronic systems is greater than that of conventional ovens; electronics are simply more expensive than sheet metal and pipes. The economic benefits of all capital equipment come with use, not ownership. EGI's leasing policy reduces capital expense and permits the acquisition of an entire system while not having to be concerned with technical obsolescence. The numerous other advantages to a printer can be learned from any comptroller of any major corporation. More important than capital costs are the costs of consumables. In minimizing these costs, Electricure electronic systems are unequaled. Consider the following variable costs:

1. Energy--Lower utility costs because of reductions in usage of electricity, gas, water, etc., required for drying, cooling, incineration, and recovery of solvents. (Freedom from dependence on natural gas is invaluable in itself.)
2. Productivity--Increased production from faster presses, quicker make-ready, and less down time.
3. Ink--Less waste and greater mileage with somewhat higher ink cost per pound, resulting in lower ink invoice costs.
4. Waste--Slaved drying response and instantaneous response produce less scrap paper.
5. Paper--Thinner grade and lower coating-weight papers are permissible with compact cold ovens that use inks that dry before they penetrate.

6. Labor--More effective use of manpower, resulting from automatic operation. Complete cost models have been prepared for various printing processes, but even though figures don't lie, liars can figure, so we prefer that these computations be prepared by you; we offer our assistance only.

Safety

Electricure electronic systems eliminate heat, fumes, and fire hazards from the pressroom. They meet OSHA requirements, national electrical codes, and State regulations. Pressrooms can thus become safer as well as more pleasant work areas.

I would like to pause after this exposé of all of the virtues of Electricure electronic systems and comment on the disadvantages.

Pride

Electri Graphics is not a major corporation but has hit the industry with what has been referred to as "fantastique, the greatest invention since Gutenberg, magic." The NIH (not invented here) effect on research directors has been for some to fund their own research and rediscover electron drying in their own laboratories. Their game plan is simple: prove what has been demonstrated by EGI; assemble reports dating back 20 years to show that they were not inactive these past years; piously ponder the engineering difficulties of high-energy electronics, aerodynamics, and printability of this new technology; recognize the inevitable by postulating that it is 5 to 10 years away; then pride themselves with the rapid success of their own developments. The realization that no one has a monopoly on talent is difficult to acknowledge when you are responsible for large research budgets.

Hangup

The U.S. printing industry has a hangup: UV. The vast amount of dollars spent on research, engineering, equipment, and promotion by a large number of companies, including chemical companies; ink, lamp, and press manufacturers; and printers can not be justified. The meager sales of UV inks--less than 1 percent of the market--are a measure of the actual printing after 10 years of commercial exposure. The effort to make this low-energy source do the impractical has been horrendous. As with all hangups, preoccupation with UV is hard to identify, painful to acknowledge, and persistent. Perhaps at one time the effort was worthwhile in order to prove that that new technology could do new things, but that time has passed. The abandonment of all further UV research by a number of industry leaders at a time when there are more manufacturers of equipment than ever (11) is a good omen.

Credibility

We live at a time when cynicism is a daily fact of life. Deceit in business and private and public life is common and causes all to doubt most statements. The newer, the more significant the development, the greater the doubt. We are delighted to demonstrate the scientific validity of all of our statements, but so often justification for doubts is what is sought. Scientists also have lost credibility. Perhaps in 1985, after 10 years of commercial installations, this doubt will disappear.

Money

When venture capital was needed by the manufacturer of our accelerator to prove the concept on a commercial level, high interest rates dried up venture capital more severely than it did research budgets. The problems of tomorrow were forgotten for the problems of today. This injury caused delay but shifted electron technology to EGI, and we now captively manufacture the entire Electricure system. With the delay behind us, our technical strength is greater.

Risk

The capital cost of large electronic systems is high. This makes the gamble large, and doubting people become cautious. The thrill of being first is lost to the necessity of being safe inside the fold. From that position, one can complain about EPA regulations, OSHA inspections, energy interruptions, and material shortages, and still do nothing and not be noticed. To the real leaders, not necessarily the big printers, this is nonsense, and explains why their profit margins are greater. With more expensive, yet more productive equipment, and consequently with lower cost, these firms grow at the expense of other larger, more ponderous ones.

I would like to apologize for straying from the environmental effects of our Electricure system. It is difficult to find more to express after one has demonstrated zero pollution, except that partial solutions become inadequate. Incinerators, afterburners, smoke precipitators, dust collectors, and solvent recovery plants become inadequate and obsolete before they are purchased.

REFERENCES

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2. "Cathode Ray Emission System," Paperboard Packaging, October 1974.
3. "Electricure^{TM} Images of the Future," Gravure Technical Association Bulletin, Summer 1975.

COMMENT

CHAIRMAN DOWNIE: I am struggling hard to find what Bob's talk illustrates. I think maybe it illustrates the ingenuity of American industry to respond to a challenge. I think it might illustrate serendipity, where you fall into something ghastly and come up covered in diamonds.

I think it illustrates that if I had seen his paper first, I think I would have asked the first two speakers not to bother. I will tell you what I am going to do. I am going to change my name from Bob to Thomas because that is exactly what I am. I am sorry, Bob, I am a much doubter. What a bloody awful talk.

CARBONLESS COPYING PAPERS

George Baxter, Ph.D.*

Abstract

The application of microencapsulation technology to pressure-sensitive copying systems in modern manifold business forms has grown dramatically in the past few years. It appears tht the higher cost and higher waste during forms manufacture with such systems have become less significant factors in curtailing their use than they were formerly. The improved quality and cleanliness of the copy obtained with microcapsule systems as compared with the older hot melt wax (carbon paper) systems is only a partial explanation for their wider use. Short supply of raw materials, preservation of the ecology, and waste disposal are now serious considerations limiting the use of the older pressure transfer copying systems. The technical and economic feasibility of recycling carbonless copying papers after use has been demonstrated and this is an additional attractive feature of such systems.

INTRODUCTION

The most widely used copying system in business forms today is still carbon paper. This term covers a multitude of pressure transferable, mark-producing coatings. The most common system utilizes wax-based coatings containing carbon black or other pigments (figure 1). Such coatings are of necessity relatively soft and of low tensile strength and they tend to be dirty to handle. Also, they are prone to premature transfer in the business form as the result of accidental scuffing, or the impressed image itself is liable to smudge and offset onto hands or clothing. A few of these difficulties have been avoided by the development of certain more coherent pigment-containing coatings that will transfer only to specially treated adjacent

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*Manager, Chemical Development, Moore Business Forms, Inc., Niagara Falls, New York.

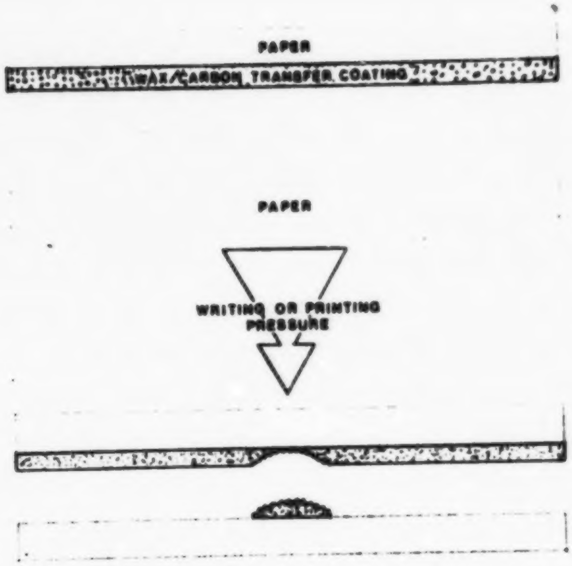


Figure 1. Image formation by pressure transfer of hot melt carbon coatings.

surfaces, but there still remain many problems associated with the use of these continuous, pressure-transferable coatings.

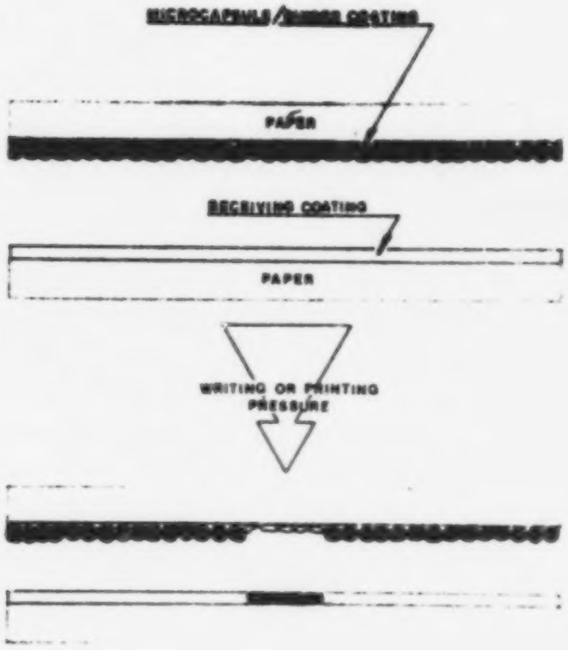
In addition to the functional and aesthetic shortcomings of carbon papers, certain other adverse pressures have been applied in recent years. Emphasis on the preservation of the ecology has had a very significant effe In the great majority of these systems, carbon is coated on tissue and inte leaved between the bond papers receiving the copy. When such forms are decollated after use, the problem of carbon paper disposal remains. No longer can these materials be incinerated in the downstairs furnace, buried in the backyard, or discarded as carelessly as before. Frequently, a significant cost is involved in their satisfactory disposal after use. Also, increasing pressure is being applied to manufacturers of carbon or other pigments to clean up their manufacturing operations. This has lead to the shutdown of several such plants with resultant supply problems to carbon paper manufacturers. Other raw materials used in this industry have also been withdrawn for ecological or toxicity reasons. The strong dependence on petroleum products has introduced additional difficulties; I will not elaborate on these. The carbon copying system which has served so well will in the future have a reduced role in our ecology-conscious society.

The newer, more efficient, microcapsule copying systems have not as yet been widely used. High cost of materials plus high waste in forms manufacture have priced them well above the carbon systems. However, as more efficient and more elegant ways are developed to manufacture and process these carbonless systems, and the problems with carbon paper persist, the price difference between the two will be minimal. A great deal of work has already been done to make the carbonless systems more economically and ecologically acceptable. The technical and economic feasibility of recycling carbonless copying papers has also been demonstrated and is an additional attractive feature of such systems.

The function of the microcapsule coatings in carbonless copying may be illustrated by figure 2. When writing or printing pressure is applied to the coated sheet, the capsules are ruptured and liquid marking fluid is transferred to the receiving sheet, making a sharp, smudge-free copy. However, during the usual handling such as cutting, perforating, punching, etc., which such papers must undergo in their assembly into business forms, the capsule coatings are prematurely damaged. This results in lower copying efficiency and, frequently, discoloration of the business forms as the result of smudging and offset. This problem has been minimized by the introduction of certain inert materials into the microcapsule coatings (figure 3). The particle size of these materials is slightly greater than that of the microcapsules and they act as "spacers," minimizing premature damage to the microcapsules as a result of incidental pressure or abrasion.

MICROCAPSULE STRUCTURE

Microcapsules can have a variety of physical structures but the present discussion will be confined to the two shown in figure 4. Figure 4a shows a capsule in which A is the encapsulated material. All of the


MICROCAPSULE/BINDER COATING
PAPER
RECEIVING COATING
PAPER
WRITING OR PRINTING PRESSURE

igure 2. Image formation by pressure transfer from microcapsule (carbonless) coatings.

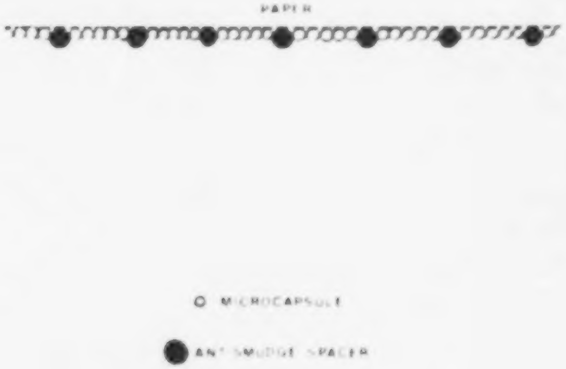

PAPER
MICROCAPSULE
ANTISMUDGE SPACER

Figure 3. Antismudge materials in carbonless copying.

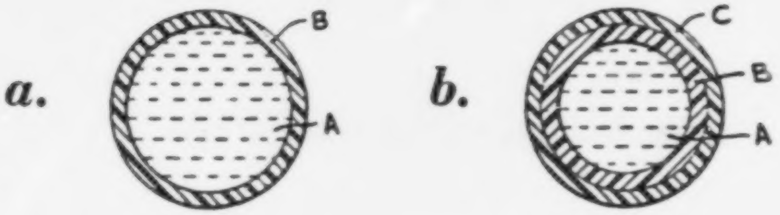


Figure 4. Physical structures of microcapsules.

processes to be discussed encapsulate a liquid core which is preferred in copying systems because of its superior pressure transfer characterisitcs in comparison with solid or semisolid core materials. B is the capsule shell material, generally a high-molecular-weight polymer. Figure 4b shows a double-or dual-walled microcapsule. Again A is the encapsulated core material, B is the inner shell wall, and C is the second or outer shell wall, generally applied by a technique different from that for the inner shell.

MICROENCAPSULATION: MATERIALS AND TECHNOLOGY

In the following discussion, the objective will be to provide an understanding of the unique advantages of the microencapsulation technique in carbonless copying, with some minor references also to its application in other areas. Those areas include the food, pharmaceutical, cosmetic, chemical, petrochemical, and bioengineering industries.

Microcapsules can be described under three main headings:

1. Microcapsule wall materials,
2. Liquids suitable for microcapsulation, and
3. Applications for microencapsulation.

Figure 5 lists capsule wall materials ranging from the naturally occurring gelatin and zein to waxes, resins, and synthetic polymers. Many other materials could be added to this list, including inorganic materials like sodium silicate. In figure 6 there is a partial listing of liquids that can be encapsulated by some or all of the wall materials in figure 5. Again, this

GELATIN
GUM ARABIC
POLYSTYRENE
ALBUMIN
WHEAT GLUTEN
ZEIN
CARNAUBA WAX
BEESWAX
POLYESTER
MONTAN WAX
PARAFFIN WAX
POLYETHYLENE
POLYAMIDE
METHYLCELLULOSE
CELLULOSE NITRATE
CELLULOSE ACETATE PHTHALATE
POLYMETHYL METHACRYLATE
STARCH ACID ESTERS
POLYVINYL ALCOHOL
POLYVINYL PYRROLIDONE
PHENOL-FORMALDEHYDE
UREA-FORMALDEHYDE
POLYSULFONAMIDE
CANDELLILA WAX
POLYCARBONATE
POLYURETHANE
POLYUREA

Figure 5. Microcapsule shell wall materials.

OLIVE OIL
COCONUT OIL
CASTOR OIL
CORN OIL
SOYBEAN OIL
WHALE OIL
LEMON OIL
ORANGE OIL
TOLUENE
XYLENE
TURPENTINE
PENTANE
HEXANE
OCTANE
DIOXAN
CYCLOHEXANE
KEROSENE
PETROLEUM ETHER
PETROLEUM NAPHTHA
MINERAL OIL
ETHYL ACETATE
BUTYL ACETATE
DIMETHYL PHTHALATE
DIBUTYL PHTHALATE
TRICRESYL PHOSPHATE
SILICONE OIL
METHYL SALICYLATE
CARBON TETRACHLORIDE

Figure 6. Liquid core materials for encapsulation.

listing is not complete and many more materials could be added. The reasons and applications for microencapsulation are many and are limited only by the imagination. In general, microcapsules are used most advantageously to protect their contents from air, moisture, microorganisms, and other contaminants. In this way, shelf life is increased and spoilage reduced. The contents may be released by breaking, crushing, melting, dissolving or in some way rupturing the skin. In some cases also the shell may allow the slow, prolonged release of its contents by diffusion through the wall, or by decomposition of the wall in certain environments. Certain other applications may require that the microcapsule contents be retained permanently within the shell walls; this is also possible. Capsule walls resistant to acid can be adapted to dissolve and release their contents in an alkaline environment. Wall materials can be designed to allow the passage of some materials, while selectively blocking out others. With

CARBONLESS COPYING
DYESTUFFS
ADHESIVES
FERTILIZERS
INSECTICIDES
PESTICIDES
FLAVORS
FRAGRANCES
CLEANERS
VITAMINS

FOOD PRODUCTS
CURING AGENTS FOR RESINS
TOBACCO PRODUCTS
DURABLE-PRESS FABRICS
DENTAL PRODUCTS
PHARMACEUTICALS
ANIMAL FEED SUPPLEMENTS
PAPER MAKING
MEDICINAL PRODUCTS
LIGHT-SENSITIVE PHOTOGRAPHIC MATERIALS

Figure 7. Applications of microencapsulation technology.

microcapsule applications, if you can visualize it, you can do it!

Some possible applications of microencapsulation technology are shown in figure 7. Many applications in these areas are aleady in use, many are in advanced stages of development, and many more will develop in the future. The technology of encapsulation is surely one of the most exciting developments of our time, and its fullest potential has yet to be realized.

REQUIREMENTS OF MICROCAPSULES FOR USE IN CARBONLESS COPYING

The encapsulation processes described here were developed principally for business forms applications which limit the microcapsules' size to the 1-10 microns range (figure 8). There is no reason why these processes could not be modified or adapted to produce a larger sized capsule, however. In all of the processes, the first step is to produce a stable emulsion of the material to be encapsulated in a continuous phase comprising the film former, or a component of the film former material capable of forming the shell of the capsules. It is also desirable to have the microcapsules in the form of a dry, free-flowing powder for ease and versatility of application to paper or other substrates. This can generally be achieved with these processes by spray-drying or by simple filtration and drying in some cases.

Microcapsule Size Range 1-10 microns

Non-Porous Thin Shell

Brittle Shell, Rupturable Under Pressure

Abrasion-Resistant Shell

Shell Inert To Encapsulated Materials

Shell Resistant To Environmental Changes

Biodegradable Shell

Figure 8. Microcapsule requirements for carbonless copying.

The essential characteristic of the film former, of course, is that it be insoluble in the material to be encapsulated. Also, the capsule wall should be nonporous, to contain and protect the active capsule contents, and abrasion resistant, to prevent premature rupture due to incidental scuffing. A capsule wall having the physical characteristics of an egg shell would be a fairly ideal structure. The capsule wall should also protect the contents from environmental factors such as humidity and temperature variations, and from the possible presence of other reactive or potentially harmful materials. All of the processes to be discussed encapsulate a liquid core since this is preferred in copying systems due to its superior pressure transfer characteristics in comparison with solid or semisolid core materials.

MICROENCAPSULATION USING COACERVATION TECHNIQUES

Coacervation is a phenomenon observed in colloid systems whereby a phase separation into colloid-rich and colloid-poor layers takes place. It may be considered as an intermediate stage in the precipitation or flocculation of the colloid material from solution. Coacervates are colloid-rich solutions (1).

The phenomenon of coacervation of hydrophilic colloids has been utilized to produce microcapsules. Oil is first dispersed in small droplets in an aqueous phase containing the hydrophilic colloid to produce a stable emulsion. At this point, the hydrophilic coacervate is caused to deposit around the individual droplets; later steps dehydrate and harden the coacervate to form a coherent shell around the droplet.

Figure 9 illustrates the process of encapsulation by simple coacervation induced by the addition of a salt solution (2). The coacervate layer deposits around the oil droplets as a fairly fragile coating which is then hardened by pouring the mixture into water at a lower temperature, to gel and set the colloid. The capsules can then be permanently hardened by a suitable chemical treatment.

Another technique of encapsulation utilizes a method of complex coacervation (3). This process makes use of the fact that two hydrophilic colloids in an aqueous sol develop opposite electric charges at certain concentration and/or pH, and coacervation takes place. Here again, the

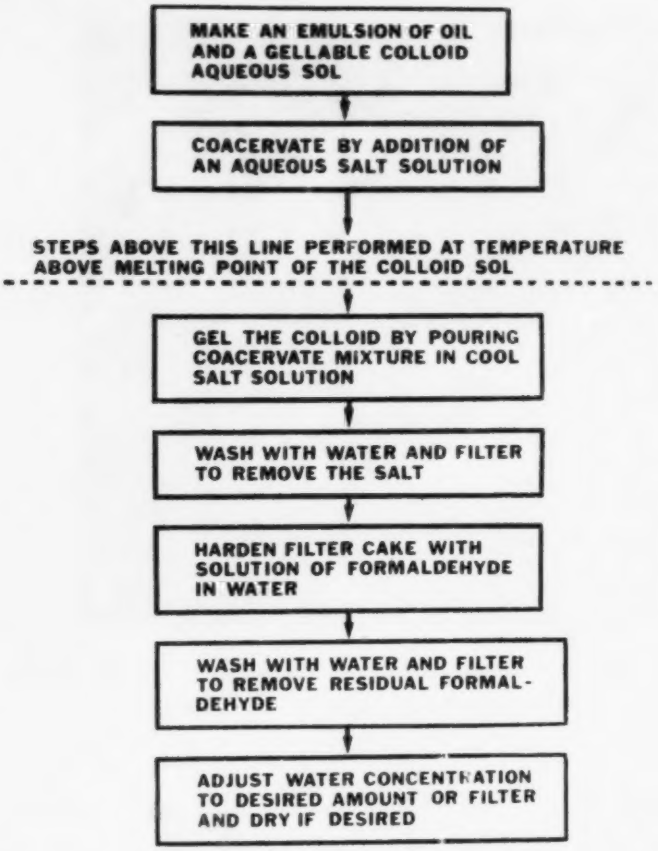

MAKE AN EMULSION OF OIL AND A GELLABLE COLLOID AQUEOUS SOL
COACERVATE BY ADDITION OF AN AQUEOUS SALT SOLUTION
STEPS ABOVE THIS LINE PERFORMED AT TEMPERATURE ABOVE MELTING POINT OF THE COLLOID SOL
GEL THE COLLOID BY POURING COACERVATE MIXTURE IN COOL SALT SOLUTION
WASH WITH WATER AND FILTER TO REMOVE THE SALT
HARDEN FILTER CAKE WITH SOLUTION OF FORMALDEHYDE IN WATER
WASH WITH WATER AND FILTER TO REMOVE RESIDUAL FORMALDEHYDE
ADJUST WATER CONCENTRATION TO DESIRED AMOUNT OR FILTER AND DRY IF DESIRED

Figure 9. Simple coacervation by salt addition.

coacervation is performed at a certain temperature, followed by gellation at a lower temperature and hardening of the coacervate layer around the oil droplets. Figure 10 shows a photomicrograph of microcapsules produced by a coacervation technique and coated on paper.

MICROENCAPSULATION BY AREA-FORMALDEHYDE CONDENSATION

Liquid droplets can be encapsulated within a water-insoluble, nonthermoplastic synthetic polymer by chemical condensation of a water-soluble resin from an emulsion continuous phase (see figure 11). The marking fluid

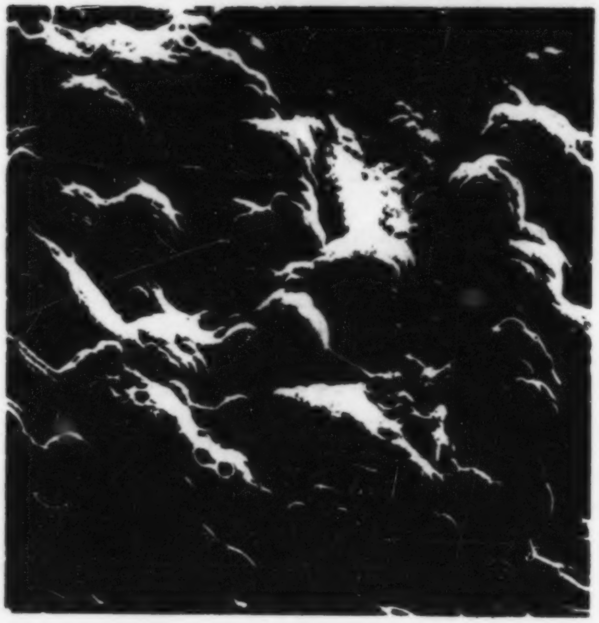


Figure 10. Electron photomicrograph of coacervation microcapsules coated on paper.

(oil) is emulsified in an urea-formaldehyde solution at room temperature. The stable emulsion is then acidified and heated to promote the condensation of the urea-formaldehyde resin material forming a tough, water-insoluble shell around the emulsion oil droplets. The resultant microcapsule slurry may then be neutralized and stored; or the capsules separated by filtration or spray-drying to produce a free-flowing powder (4). A photomicrograph of capsules prepared by this technique is shown in figure 12.

MICROENCAPSULATION BY INTERFACIAL POLYCONDENSATION

This process (5) makes use of a modification of known interfacial polycondensation techniques to produce a thin, high-molecular-weight polymer film as the capsule shell. These techniques are well described in the literature references appended to this paper (6-19). Essentially, the process comprises bringing two reactants together at a reaction interface where polycondensation occurs virtually instantaneously to form a thin film

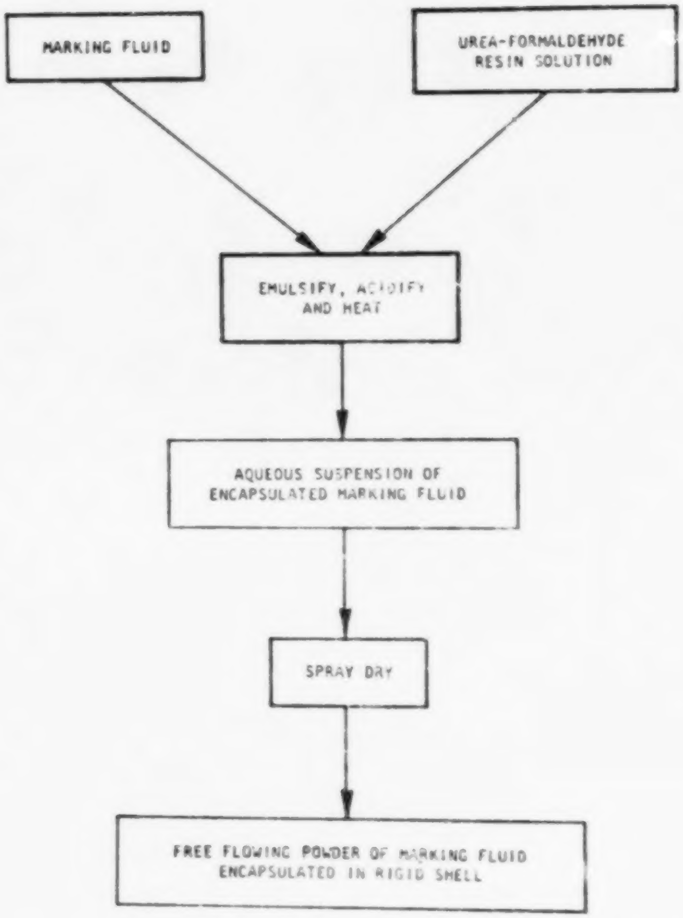

MARKING FLUID
UREA-FORMALDEHYDE RESIN SOLUTION
EMULSIFY, ACIDIFY AND HEAT
AQUEOUS SUSPENSION OF ENCAPSULATED MARKING FLUID
SPRAY DRY
FREE FLOWING POWDER OF MARKING FLUID ENCAPSULATED IN RIGID SHELL

Figure 11. Microcapsule formation by condensation of a water-soluble resin as emulsion continuous phase around liquid core droplets, followed by spray-drying.

insoluble in the parent media of the reactants. The polycondensation technique can produce a capsule shell consisting of high-molecular-weight polymer insoluble in organic solvents and infusible at hot melt coating temperatures. A particular advantage of the process also is that it provides a method of encapsulating water or water-soluble substances. Figure 13 shows some classes of polymer which can be prepared by this technique and which have been used in encapsulating a variety of materials.

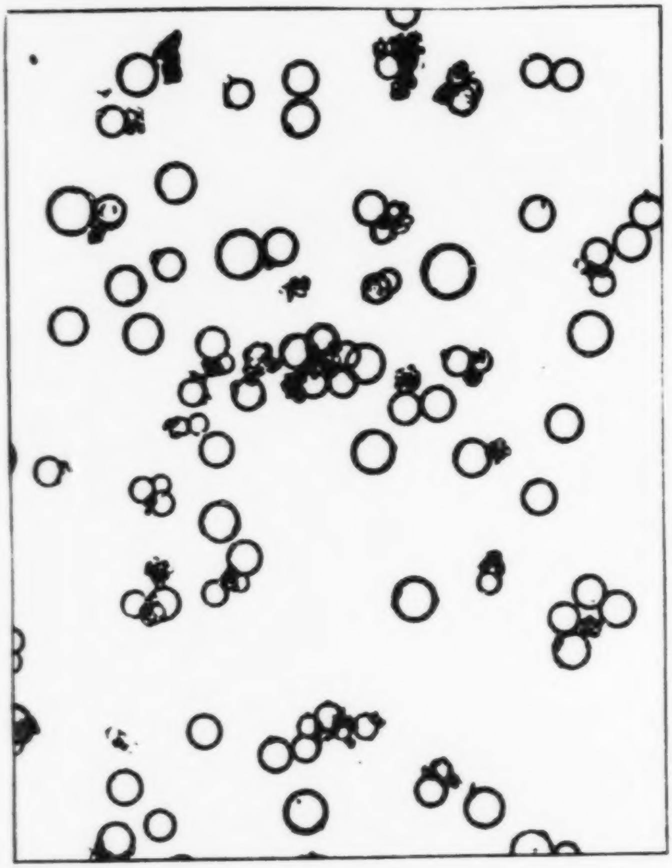


Figure 12. Photomicrograph of urea-formaldehyde microcapsules prepared by condensation and spray-drying.

The interface for the reaction is provided by emulsifying one reactant for the condensation polymer in a continuous phase containing the second reactant. The substance to be encapsulated will also be contained in the dispersed phase. However, in order to control the formation of the capsules, one reactant for the condensation polymer, together with the substance to be encapsulated, is first emulsified in a continuous phase, and thereafter an additional continuous phase containing the second reactant is added to the emulsion. The polymer shell will then form at the interface of the dispersed substance and encapsulate the material.

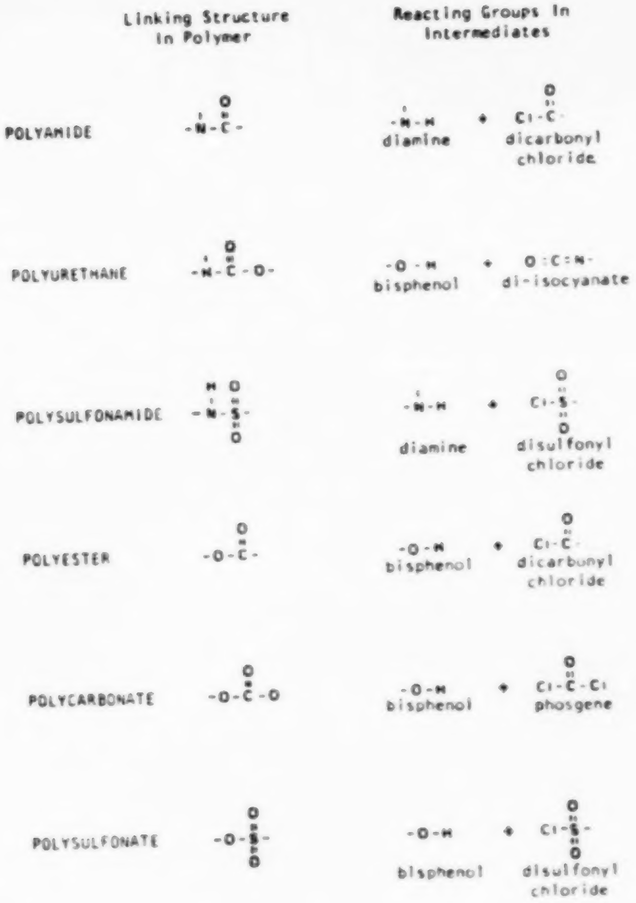

Linking Structure in Polymer
Reacting Groups In Intermediates
POLYAMIDE
diamine
dicarbonyl chloride
POLYURETHANE
bisphenol
di-isocyanate
POLYSULFONAMIDE
diamine
disulfonyl chloride
POLYESTER
bisphenol
dicarbonyl chloride
POLYCARBONATE
bisphenol
phosgene
POLYSULFONATE
bisphenol
disulfonyl chloride

Figure 13. Chemical classes of polymers useful in microencapsulation by interfacial polycondensation.

Figure 14 shows the sequence of steps in this encapsulation process. Microcapsules prepared by this method are shown in figure 15 as seen through the microscope. Figure 16 is an electron photomicrograph of the same microcapsules coated on a paper substrate.

For pressure-sensitive copying systems, it is desirable to have microcapsule walls which are impermeable to the encapsulated solvent. Where pesticides, fertilizers, perfumes, or other functional ingredients have been encapsulated, it may be desirable to have a controlled degree of

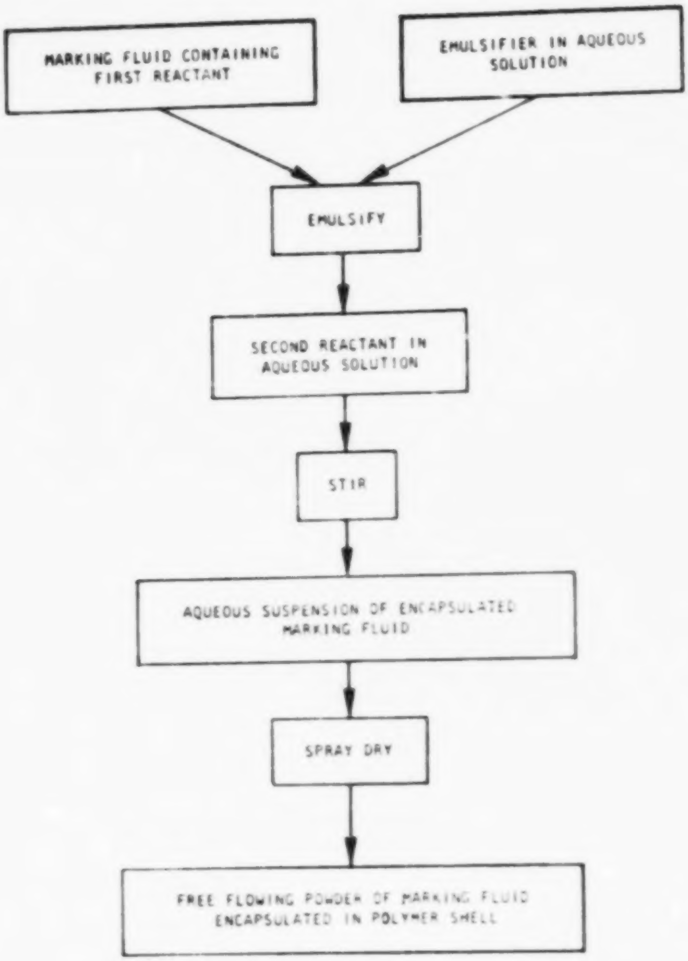

MARKING FLUID CONTAINING FIRST REACTANT
EMULSIFIER IN AQUEOUS SOLUTION
EMULSIFY
SECOND REACTANT IN AQUEOUS SOLUTION
STIR
AQUEOUS SUSPENSION OF ENCAPSULATED MARKING FLUID
SPRAY DRY
FREE FLOWING POWDER OF MARKING FLUID ENCAPSULATED IN POLYMER SHELL

Figure 14. Microcapsule formation by interfacial polycondensation.

porosity or permeability in the capsule walls to allow the slow release of the encapsulated materials. The versatility of this process allows such control over the final product. For example, experiments in our laboratories have shown that encapsulated volatile solvents such as toluene and xylene can be contained without measurable loss at temperatures close to their boiling points for periods in excess of 24 hours. Alternatively, the capsules can be designed to lose 10 percent, 20 percent, 30 percent or more of encapsulated ingredient under the same conditions and over the

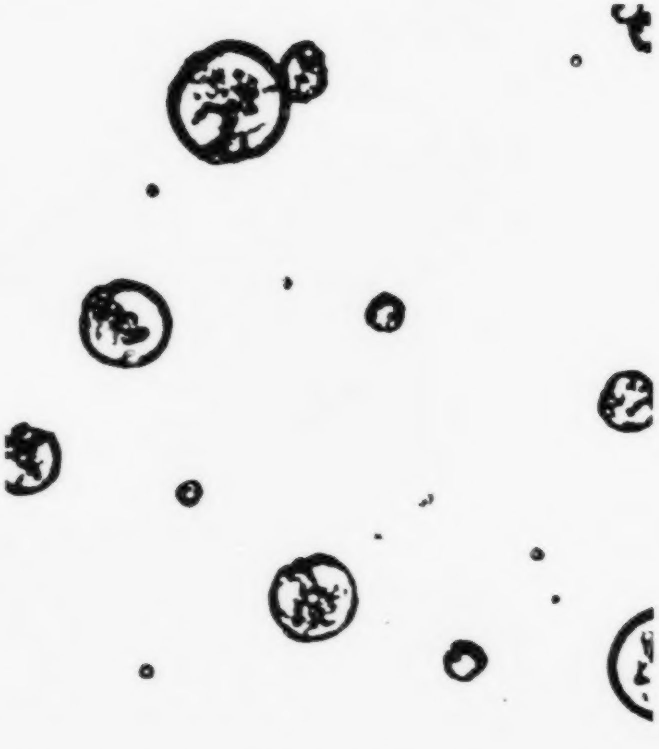


Figure 15. Photomicrograph of interfacial polycondensation microcapsules.

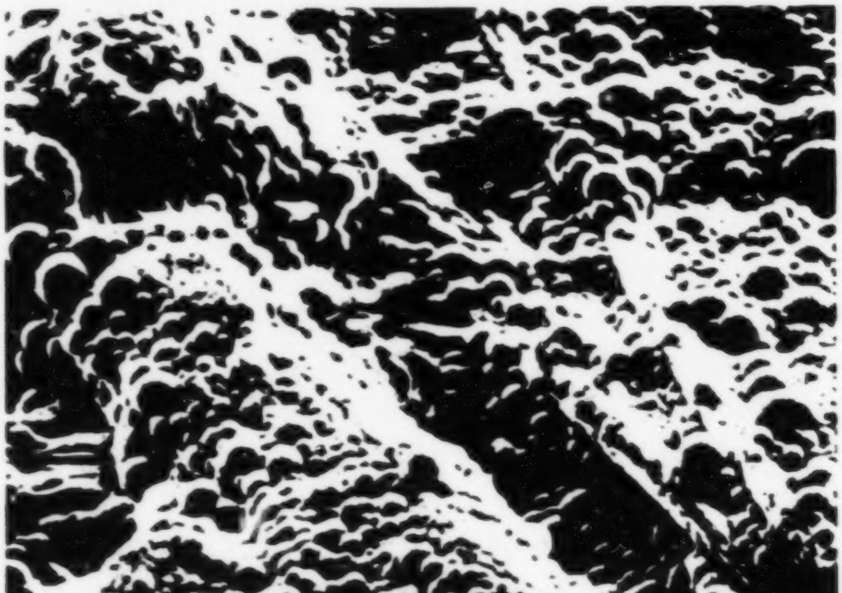


Figure 16. Electron photomicrograph of interfacial polycondensation microcapsules coated on paper.

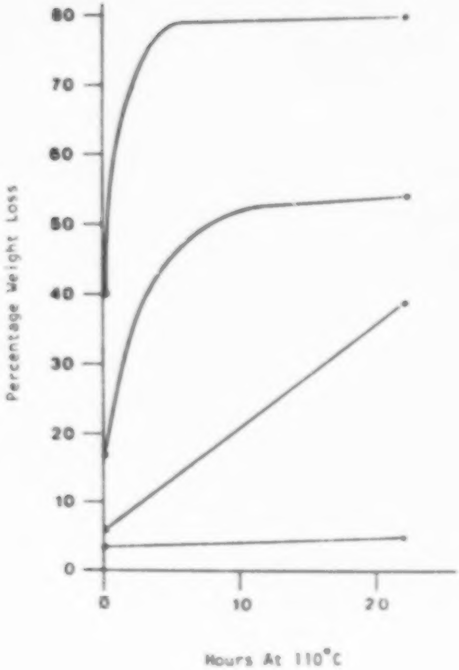


Figure 17. Loss of xylene from interfacial microcapsules at 110° C.

same time period. Figure 17 shows data obtained by this technique indicating the control that can be exercised over the capsule wall permeability.

The efficiency of encapsulation is measured by determining the amount of unencapsulated or "free" solvent. The free solvent is extracted from the capsule slurry by mixing it with an inert extracting solvent. The quantity of free solvent in the extracting medium is then measured by either gas or liquid chromatographic techniques. The total solvent in the system is determined by extracting the capsule slurry with a reactive agent, which will remove the solvent through the capsule walls. The amount of total solvent is also determined by gas or liquid chromatography. The ratio of free solvent to total solvent is the percent of free solvent and a measure of the encapsulation efficiency. The polycondensation process can be controlled at an encapsulation efficiency of at least 98 percent quite readily.

Water can also be encapsulated by this process. In one technique, a solution of one reactant in water can be extruded into a solution of the second reactant for the condensation polymer in a water-immiscible solvent, forming small droplets of water within the solution and instantaneously encasing them in a polymer skin that forms at the interface. A second technique consists of forming a water-in-oil emulsion or dispersion and thereafter adding a solution of the second reactant in oil. The reaction at the interface will encase the water within a polymer shell.

It is interesting to note that microencapsulation can be effected by this technique so as to yield capsule walls which may be safely ingested. Recently, pesticides encapsulated by this technique have been approved by the Environmental Protection Agency for first commercial marketing (ref. 20). The microcapsules were approved for use on cotton, alfalfa, and corn, and provide slow, controlled release of pesticide by diffusion through the capsule walls. This approach offers safer, more efficient, more economical, and more controlled use of pesticides.

DUAL-WALLED MICROCAPSULES

Dual-walled microcapsules, in which the wall or shell is constructed of two thicknesses of material, usually of different chemical constitution, have been prepared in several different ways. In all of these methods, however, the techniques for forming the individual walls are essentially separate and independent from one another. The processes consist of superimposing one distinct wall-forming process upon the product of another wall-forming process, each process requiring control of reaction conditions with little or no relation to the requirements of the other.

The unique feature of this process (ref. 19) of forming dual-walled microcapsules is that the technique for producing the inner wall of the microcapsule automatically initiates the process for forming the outer wall. In the first stage of the process, a proteinaceous film former is deposited from an aqueous solution around core droplets on nonaqueous solvent in an emulsion as the result of a reaction with a protein-insolubilizing reactant in the core droplets. Acid is released as a byproduct of this reaction, lowering the pH of the aqueous emulsion phase. A second hydrophilic colloid in the aqueous phase then undergoes coacervation with the remaining proteinaceous colloid upon reduction of pH to within a predetermined range, and thus an outer skin is formed on top of the first. This complex coacervation mechanism was discussed earlier and is well documented in the patent literature and elsewhere (refs. 1,3).

The procedural steps for making dual-walled microcapsules by this method are shown in figure 18. Following the emulsification step, a thin film or skin can be observed around each droplet on microscopic examination. When a sample of these droplets containing mineral oil, for example, is air-dried on a microscope slide and immersed in toluene, little or no oil is extracted. This confirms that the inner wall has formed as an impermeable layer around the oil droplets. When the product after the

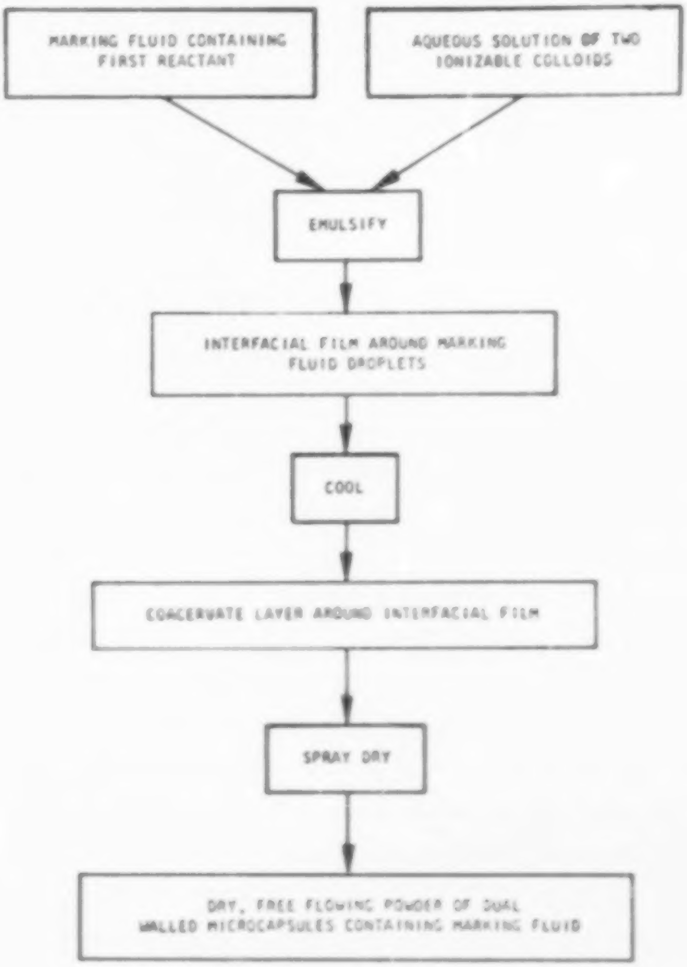
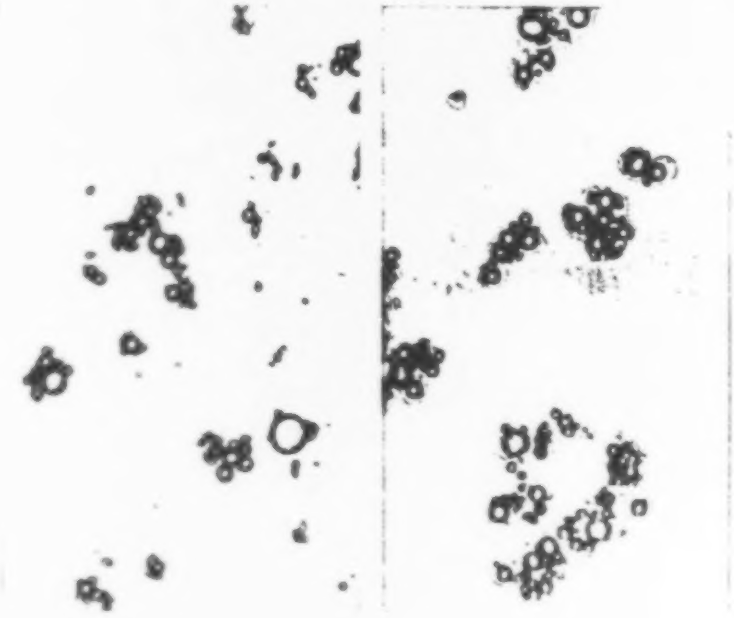

MARKING FLUID CONTAINING FIRST REACTANT
AQUEOUS SOLUTION OF TWO IONIZABLE COLLOIDS
EMULSIFY
INTERFACIAL FILM AROUND MARKING FLUID DROPLETS
COOL
COACERVATE LAYER AROUND INTERFACIAL FILM
SPRAY DRY
DRY, FREE FLOWING POWDER OF DUAL WALLED MICROCAPSULES CONTAINING MARKING FLUID

Figure 18. Dual-wall microcapsule formation.

cooling steps of the process is examined microscopically, the formation of the second wall layer can be seen. This wall has a considerably greater thickness than the inner wall and is gelatinous in appearance--it can readily be distinguished from the inner wall under the microscope. Samples of such microcapsules containing mineral oil have been immersed in hot toluene for up to 2 hours; the washed samples released copious quantities of oil under pressure. Also, similar microcapsules can contain xylene at temperatures close to its boiling point without appreciable loss. Figure 19 shows single-walled microcapsules after the first shell-forming reaction, and dual-walled microcapsules after the coacervation step.



(a) Single wall. (b) Dual wall.

Figure 19. Single-walled microcapsules after the first shell-forming reaction (a), and dual-walled microcapsules after the coacervation step (b).

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SESSION SUMMATION

Robert H. Downie
Session Chairman

I think what you have heard today illustrates a number of things. I think you have gained an insight into the developmental cycle of some processes that are going on in the graphic arts and some understanding and appreciation of the painstaking step-by-step compromises that have to be made.

We have illustrated among ourselves the healthy competition of technologies and the range of options open to us. We have described some methods that we are using to tackle the problems that are raised by the environment. Also illustrated were the agonies of the trading of properties that go on. One aspect that possibly was not evidenced was that the cost of development described in these four papers, when added together, has to be in excess of $25 million. The level of activity has been impressive. It always impresses me that the pressure from the marketplace has often run far ahead of any pressure that we get from any other source. A lot that you fellows talk to us about, and one of the understandable agitations we get, is that we often feel as though you're teaching your granny how to suck eggs.

We do appreciate the role and the task that we all have. We are applying ourselves most diligently to tackling it. I work very diligently with the Environmental Conservation Board of the Graphic Arts, which is a group of large printers who got together to work in tackling our problems with the environment. I happened to chair the OSHA committee of that Environmental Conservation Board, and I have been very gratified at the progress and the accomplishment that we have had in 2 brief years, with volunteers on that committee meeting once every 2 months. A little thing that came back to me was that if a first-rate company has a first-rate insurance company monitoring what it is doing, it is awfully close to doing what OSHA requires and OSHA regulations are no great problem to meet. I am comforted that, as we come to appreciate each other's viewpoint and start to get a hands-on relationship with problems, many of the seeming ideological or practical differences will disappear.

24 September 1975

Conference Summation

Farley Fisher, Ph.D.
General Chairman

CONFERENCE SUMMATION

Farley Fisher, Ph.D.
General Chairman

This concludes our conference. I hope you have all learned something: maybe not as much as I have, but I hope you have all found it profitable.

Before we close, I would like to express my appreciation to our four session chairmen: Dr. Burachinsky, Dr. Schaeffer, Mr. King, and Mr. Downie; and to our roster of speakers who I think have done a very nice job of presenting us with an awful lot of material. I would also like to thank all of you who attended, who participated from the floor, asked questions, and made comments. I would like to thank the staff of the Holiday Inn, Valley Forge, for their cooperation and the facilities they provided us, and the Montgomery County Convention and Visitors Bureau for their assistance in manning the registration desk and helping some of us out with some arrangements. I owe thanks to a few organizations who gave us considerable assistance in putting this program together: the Graphic Arts Technical Foundation, the Gravure Research Institute, the Association of Photographic Manufacturers, the National Association of Printing Ink Manufacturers, and the Printing Industries of America.

At this point, I am supposed to give some general summation and impressions from the conference. This is always very embarrassing because, I am told that I am to summarize a conference, but I am not to say anything that might be interpreted as a government policy. So, I have to make that caveat and say that I am speaking for myself. I am not the kind of person who can sit here for 2-1/2 days and immediately have everything figured out and know exactly what it all means. I have to go home and sit down with the record and think about a lot of the things I have heard.

I do have just a couple general impressions that I will share with you. One is that I really have the impression, Dr. Muggli's comment notwithstanding, of an industry which, at least on the surface, is really quite innovative. It is not an industry that is opposed to new techniques and new ways of doing things. This impresses me because I know of a lot of industries of which that simply is not true. I think that this innovation holds out a very great promise, but we have to remember it also carries with it an attendant risk. This is true environmentally as well as economically. Every new advance is somewhat untried. No matter how much we worry about it, no matter how much we test it out beforehand, no matter how much thought and commiseration and debate we have, whenever something new really comes into use we find out things about it we just did not know before.

And so we do have to keep our guard up. We do have to take all the care we can. And we really have to trust a little bit to luck if we are going to improve, to make a better future and not a poorer future for ourselves and the people who follow us.

I also have the feeling that the industry is at least aware of some of its problems, and those it is aware of, it is making a serious attempt to deal with.

It is also very instructive that we have learned that people who made environmental improvements as recently as 5 years ago, despite the advice of their bankers that it was a waste of money, have found themselves coming out smelling very nice in the money market. This tells us something that I think any third grader knows but which we tend to forget when we grow up; namely, that waste is waste.

All this stuff that EPA, the various States, and other people are complaining about dumping in the environment because they don't like it there is in many cases useful stuff. Throwing it away is just not a commonsense thing to do. We have to make an effort. After all, the best way to deal with waste is to realize that it need not be a waste, that maybe it is a useful commodity in its own right. I think we have seen some very good examples of that here, and I hope that we can keep on moving in this direction.

I've probably said enough for the time being. Before I adjourn the meeting, however, I would like to open it up for comments from the floor for one last time, in case anybody does have something they have not had a chance to say up to now.

MR. FREDERICK WOOTTON (Prince George's County Health Department, Cheverly, Maryland): I have sat here for 2-1/2 days and have enjoyed it. I don't know if I really have enough information to put out. Sixty-five percent of all your taxes are going to the military. I should point out that, being a health person, I believe that possibly we could divert some of these funds to some of the research that you all have said has cost you so much.

MR. DAVID FRIEDMAN (Food and Drug Administration, Washington, D.C.): We have heard several comments by some speakers that there is an adversary atmosphere between industry and the various government agencies, and that there should be more cooperation. I want to suggest to everyone that the relationship need not be antagonistic; we are not out to "get" anyone. If industry and trade organizations would cooperate, would give us the information we need--before new developments are in progress, when new techniques are being developed--if they would work with the various environmentally active agencies, industry might be able to find out what not to do. It is a lot easier to reformulate before environmental damage, or before commitment in the marketplace, than it is afterwards. We are out to try to prevent problems, and not simply deal with them once they are known to exist.

MR. THEOPHILUS R. CARSON (Food and Drug Administration, Washington, D.C.): I would like to commend Dr. Fisher and Mr. Ayer for the wonderful job they did in getting this together as fast as they did. I had to take someone else's place; that is why I am here.

MR. AL JASSER (Anchor Chemical Company, Hicksville, New York): I want to commend you, Dr. Fisher, for the conference. I have one plea from industry. The problem you have stated at another time was that there is no communication. This young man from FDA again repeated that there should be cooperation. Industry is always willing to cooperate with government if it can understand what government wants. If the language in the Federal Register, for example, were such that my staff could understand it without lengthy conferences, we would be well along in the way of cooperation. We are very happy to cooperate. Is there something that you can do in seeing to it that the directives, orders and prospective regulations are in clear, simple language so that we in business don't have to take a special course?

GENERAL CHAIRMAN FISHER: I would point out to you, first off, that I am a chemist myself; most of the government people here, I imagine, are technical people of one type or another. Most of the industrial people here, I imagine, are technical people of one type or another--engineers, chemists, and so on. But the fact of the matter is that the government is run by lawyers. They write the Federal Register. Business is not really run by scientists and engineers either. Business is run by businessmen. I think all we can really strive to do is maintain communication at the technical level so that we at least know what we are supposed to be doing. I know it's just a plain fact of life that when you get into the higher levels of management in either government or industry, a lot of information can get obscured.

I would like to make one more comment which I have heard made privately on a number of occasions. Dr. Schaeffer and I have discussed it at some length. That is, many of these engineering advances that we have heard discussed here, many of the fancy pollution control devices, are really practical only in large installations. But, in fact, we are dealing with an industry which has an awful lot of small installations. In a sense, we have been a little unfair, because I really do not think we have addressed the problems of these small operators. Many of the things which we did discuss are not practical from their point of view. I think that is an area which requires more thought and a little more effort.

If there are no further comments, I will call the meeting adjourned. I want to thank you all for your cooperation and attendance.

Submitted Papers –
Not Presented at Conference

COMMENTS FROM A SCREEN PRINTING INK AND PRESSURE-SENSITIVE-FILM MANUFACTURER: GENERAL FORMULATIONS - DIVISION OF GENERAL RESEARCH

John H. Sommer*

Screen printing owes its existence to three qualities lacking in most other methods:

1. inexpensive short runs,
2. bright sharp colors, and
3. durable or long-lived printing for outdoor exposure.

Screen printers, and their end products to a significant extent, are different from the other branches of the printing industry. The printers themselves differ in that the vast majority of them operate very small shops with limited facilities. It is not too costly to get into the screen printing business. The end products are very often used in outdoor applications requiring relatively long life and, not infrequently, exposure to a variety of chemicals or corrosive conditions. Therefore, it is important to screen printers that they have outdoor-durable inks. This ultimately means to exclude, for examples, cadmium and lead chromate pigments. This in turn makes it difficult for the screen printer to supply durable name-plates, direction labels, and emblems. Less durable but so-called innocuous pigments could be used by overlaying the printing with a clear protective film. This is already being done to extend the life of emblems made with durable pigments. However, very few shops have the overlaying equipment, and overlaying makes a more expensive emblem and consumes more material.

Outdoor-durable screen printing inks very often necessitate solvents for vehicle systems that aid in making durable signs. These may have low MAC values and/or may be excluded on the Rule 66 basis. Ultimately, the inkmaker is limited to what the pigment, resin, and solvent producers supply to him, and even if rectified products from these producers are forthcoming, the inkmaker still has left the recompounding or formulating of ink systems and weathering tests, which is time consuming.

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*Division Vice President of General Formulations Company, Division of General Research, Inc., Sparta, Michigan.

But what is a rectified ink--an ink that is logically considered safe? As quantitative data are gathered on toxicity at all levels, what are the parameters that determine acceptability? With all the logic and morality in the world, we need facts in order to make a judgment that it is more important to eliminate cadmium and lead chromate pigments from the world than to disallow motorcycles and cars to be driven, or bathtubs to be used, or alcohol to be ingested, at least in excess.

I realize that it is the proper function of the Office of Toxic Substances of EPA to make inquiries. Along with State-related departments, it has already done and is doing, in general, a good job in having industry clean up its act, and it is delving further. I do think, though, that no one, including EPA, wants safety to reach its logical conclusion, which would be to stay in bed and reach out for food as needed. So you come to the horns of a dilemma. At what point do we say we will allow a certain percent of all living plant and animal life to die from what we call, for want of better terminology, an abnormal death or disability? Indeed, what is normal death? I ask this because when most of us hear of the death of someone we know, we often say, "Well, that person did this or that which contributed to his or her demise." What is the virtue of doubling our life spans when we are rapidly overcrowding the earth? My point is that in our society, we do allow people to conduct themselves in ways that consciously or subconsciously determine their own ends. This is the free enterprise system and if you do not like that terminology, then it is a "free democratic society." It is, however, our duty as member of so-called scientific, industrial, political, and educational societies to apprise people of their options and in as quantitative a way as possible indicate to them their chances of survival upon being exposed to this or that environment.

This precipitates the thought that life and living are horribly complicated and that a person, upon being apprised of his options, will most certainly proceed to other options--ad infinitum.

Our society is torn in several directions: 1) We are told we must conserve energy; 2) We are told to, and indeed, we wish to maintain or increase our well-being in terms of material goods and our health; 3) We are told and shown that our morality and ethics need improvement at all strata of society; 4) We are told also that we must not pollute. Our society is frustrated. We feel rotten about it. What do we do?

Nothing will be solved overnight, but it would appear that inasmuch as we do allow our fellow man to shorten his life in so many ways, it should follow that all the experts should do is advise people, as we gain knowledge, to allow them to choose their options, and, in dangerous situations institute an enforceable cessation of exposure.

Philosophers and/or religious leaders have not been very effective in guiding our lives to a high moral and ethical plane and certainly the political arena has not helped, nor apparently have the educators. It follows, therefore, that science and industry should show a selfless consciousness in upgrading the morality and ethics of our society. This does not necessarily mean we should eliminate cadmium and lead chromate pigments (again only as examples). We should join all forces in society and evaluate priorities based on their relative effects in a rational, logical manner devoid of self-interests. Then if a segment of industry suddenly becomes mortally wounded (we must admit past mistakes), that segment should be helped to rally and redirect its energies. If we do not do this, it will be a parry-and-thrust process of fighting for self-interests and we shall continue to fight each other, in a sophisticated way of course, but in a way not at all dissimilar to the cavemen. Science and industry need a new image, and what better way of achieving this image than a sincere show of altruism for mankind.

I do not think the above has been a digression from the agenda of this meeting. Rather it is a beseeching to EPA that as individuals of professions and as members of society we be given the full overview of environmental protection and what needs to be done first, second, etc. We are reasonable people and, like anyone else, upon being shown the light and being assured of no calamitous result to our workers and our companies, we will proceed in an effective way to accomplish what needs to be accomplished.

It is understood, of course, that the protection of the environment (and mankind by inference) can and should be pursued in more than one area, and I still refer to cars, motorcycles, etc., as polluters, killers, and extravagant wastes of natural resources. I may be wrong, but they do make a potential ban of lead chromate a little ridiculous.

Science and industry have eliminated many problems of environmental pollution and in the process have created new ones. For example, the transition from coal-operated engines and horse-drawn vehicles to internal combustion engine vehicles was a remarkable and revolutionary accomplishment but virtually devoid of environmental considerations.

Now, however, pollution potential or consequences are considered and it follows as night does the day that science and industry will consider the environment as a new component to be dealt with in technological advancement.

Many of us have already upgraded our plants in terms of cleaner air and lower noise levels. More is being done, but it costs money, and in a competitive society it can only proceed to the extent that competition dictates the amount of money available from profit. At the present time there is a squeeze that makes improvement difficult or minimal, and in many cases financially impossible. In fact, the impact of more and more restrictions makes it increasingly difficult for small businesses to start, and indeed for existing small businesses to continue.

In summing up our attitude, I would suggest the following approach to environmental protection as our industry affects it.

1. Assemble facts regarding mortality and injury rate per degree of exposure to each substance. Evaluate these in the full overview of protection priorities. Publish the information and above all make it readily available. To do this, prepare a confidential, not-to-be-signed questionnaire for each segment of the printing industry and for individual manufacturers. Ask them what solvents, pigments, monomers, and additives are used and what problems are encountered. Every manufacturer feels he has secret formulations and/or processes that he wants kept secret--whether this is right or wrong--and he wants any problems minimized.
2. If hard facts or conclusive ones are not truly convincing or available, then on an interim basis require raw material suppliers and ink manufacturers to list potential hazardous substances, or, do what is required of the tobacco industry: publish a disclaimer saying, "The use of this product may be hazardous to your health." This, of course, is being done, but it can be more complete. Obviously, this later approach is ineffective in stopping production of a product, but the comment does give the individual a warning and the option of not using it.
3. If conclusive facts are available and condemning, then by all means consider the problems facing the producer and user in confronting

the cease-and-desist order and assure them of aid in the transition, both technologically and economically. It is this unknown that puts us on the defensive--rightly or wrongly, this is a point that cannot be over-stressed. Asking for governmental aid is an anathema to most of us, but if our processes and procedures are interfered with, it is a reasonable socialistic request to keep the system viable.